

Université catholique de Louvain École polytechnique de Louvain Institute of Mechanics, Materials and Civil Engineering (IMMC) Institute of Information and Communication Technologies, Electronics and Applied Mathematics (ICTEAM)

Internal stress and opto-electronic properties of pure and Al-doped ZnO thin films deposited by reactive sputtering

Romain Tuyaerts

Thesis committee

Prof. Joris Proost (Supervisor) Prof. Jean-Pierre Raskin (Supervisor) Prof. Thomas Pardoen Dr. Quentin Van Overmeere Dr. Philippe Guaino Dr. Marc Verdier Prof. Renaud Ronsse (President) Université catholique de Louvain, Belgium Université catholique de Louvain, Belgium Université catholique de Louvain, Belgium PARC, USA CRM Group, Belgium Grenoble INP, France Université catholique de Louvain, Belgium

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Abstract

In modern society, more and more applications use thin film coatings to improve, or add a functionality to a substrate. A widely used category of thin films is transparent conductive electrodes (TCEs) that are used in fields such as displays, touchscreens, photovoltaic solar panels, or window glasses. Different classes of materials are possible for transparent electrodes but the most popular is doped metal oxides. Indium-Tin Oxide (ITO) is currently the material with the best properties but contains a high amount of indium, a metal that is not abundant on Earth and its extraction could become problematic in only a few decades. Therefore, it is mandatory to prepare the next generation of TCEs, with cheap and abundant materials. In this thesis we focus on zinc oxide (ZnO), that is a promising material already used in some applications such as solar panels. Different dopants can be used to make conductive ZnO, and aluminum doped zinc oxide (AZO) has here been chosen because of its good properties, and because aluminum is a cheap, abundant, non-toxic metal. The deposition technique studied in this thesis is reactive sputtering, a technique that allows to deposit thin films at room temperature on various substrates, and that is commonly used in the industry. First, the different deposition parameters are studied and their effect on the electronic and optical properties of ZnO and AZO is investigated. An insitu analysis of the internal stress during deposition provides new insight on the growth mechanisms and defects present in the thin films. An onchip technique was also optimized to test the mechanical properties of oxides thin films such as zinc oxide. Finally, an adapted process is also proposed for the testing of graphene that is also a promising material for future TCEs.

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Chapter 1

Introduction

"Thin films" refer to materials deposited in layers thinner than a few micrometers and are more and more used since the last decades. A large use of thin films is obviously electronic systems, where miniaturization is mandatory to increase the density of devices per square centimeter. This miniaturization therefore requires smaller patterns and a smaller thickness. An other large use of thin films is surface coatings. In this situation the thin film is added on top of a bulk material, or other thin films, to improve or add a functionality to the substrate.

Common uses of coatings are the improvement of the chemical resistance with an inert layer, of the wear resistance with a hard coating, (anti-)reflective coatings to change the optical properties, or electrically conductive coatings. For coatings, several applications do not require miniaturization. However the use of thin films is still used because a thinner film decreases the production costs, and is also more flexible. This flexibility is of interest for the industry that actively develops flexible electronics.

Transparent conductive electrodes

Transparent conductive electrodes (TCE) have an increasing importance in modern society in fields such as displays, touchscreens, photovoltaics or window glasses. [1] Depending on the applications, the TCEs require different properties. For displays and touchscreens, a high transparency in the visible spectrum is the most important to obtain a clear image. In photovoltaics, it must be transparent over the spectral irradiance of the Sun and for photons that have an energy higher than the bandgap of the absorber material. Low sheet resistance is also of high importance in photovoltaics to increase the yield of solar panels.

In window glass, TCEs can be used as heating elements for defrosting. It can also be used in low-emissivity coatings that control the light flux. In this case, the electric conductivity is not required but the high reflectivity in the infrared spectral range (>1 μ m) is used. [2] For windows, the cost and toxicity are important parameters so that indium tin oxide (ITO) and cadmium stannate (Cd₂SnO₄) are no longer used despite their good performances. To obtain better properties in the infrared range, stacks are also used with a metallic layer (typically ~10 nm of silver [3]) between two metal oxides such as ZnO or SnO₂. The high electronic density of the metallic layer increases the reflectivity in the IR range, while the low thickness allows to keep a high transparency in the visible spectrum.

Transparent conductive oxides

A popular class of TCEs is transparent conductive oxides (TCO). Among all available TCOs, three of them obtained a particular attention due to their large bandgaps (> 3.2 eV) and low resistivities (< $10^{-4} \Omega.cm$): SnO₂:X and ZnO:X where X is the dopant, and In₂O₃:Sn (ITO). The intrinsic bandgaps of these materials are around ~3.6 eV for SnO₂ [4], ~3.3 eV for ZnO [5], and ~2.7-2.9 eV for In₂O₃. For In₂O₃ however, the fundamental bandgap corresponds to a forbidden transition leading to low absorption. The first allowed transition leading to a high absorption is at ~3.7 eV. [6] All these bandgaps correspond to the undoped materials and can be increased by a few tenths of eV by doping, through the Burstein-Moss effect due to the filling of the conduction band. ITO often has resistivities slightly lower than the other two but they all can reach resistivities lower than $10^{-4} \Omega.cm$ in optimal deposition conditions. [7–9] For low temperature deposition however, aluminum-doped ZnO (AZO) seems to be a good candidate due to its high transparency (> 90%), low resistivity (generally slightly lower than SnO_2), low cost, non-toxicity, and good quality, even at room temperature deposition.

Alternative TCEs

Other TCEs than TCOs are available such as metal grids, dispersed metal or carbon nanowires, graphene or conductive polymers. Patterning a metal grid adds a processing step that increases the costs. However the scattering induced by the nanogrid can increase the absorption and the short-circuit current in thin film solar cells. [1] A continuous roll-toroll nanoimprint lithography has been demonstrated as a feasible high speed and large area nanoscale patterning with an improved throughput and reduced cost to obtain metal nanogrids. [10] Conductive polymer such as poly(3,4-ethylenedioxythiophene) (PEDOT) dispersed with poly(styrenesulphonate) (PSS) usually have a resistivity higher than 0.1 Ω .cm, but resistivity as low as $7 \times 10^{-4} \Omega$.cm has been demonstrated by Kim et al. [11]. PEDOT was first used as an antistatic coating and as a hole-injection layer in organic devices due to its high resistivity and work function, but with this new low-resistivity, PEDOT can now be used as an electrode in organic thin-film solar cells. [1]

Graphene could also be a good candidate for TCEs because of its optic and electric properties. Due to its extremely low thickness, it can combine a metallic behavior with an excellent transparency (T $\simeq 97.7\%$). Undoped graphene has almost no charge carrier, leading to a high sheet resistance of a few k Ω , much higher than current TCOs. However, real graphene samples contain defects and have adsorbed impurities that increase the charge carrier density. Thanks to its 2D structure and symmetry, graphene has mobilities much higher than metals or TCOs, typically of 10^3 to 2×10^4 cm²/V.s, compensating for its low charge carrier density. For example, Bae et al. demonstrated roll-to-roll process of 30inches graphene films for transparent electrodes on PET substrates. [12] The single layer graphene had sheet resistance of ~125 Ω and with a stacking of four layers, they reached a sheet resistance of ~30 Ω and transparency of 90%.

Contradiction between transparent and conductor

The difficulty to obtain good TCEs comes from the required properties (electrical conductivity and transparency) that are often opposed. Indeed, the electrical conductivity for a material with a dominant type of charge carrier is given by:

$$\sigma = en\mu \tag{1.1}$$

where e is the elementary charge, n is the charge carrier density and μ is the charge carrier mobility. Generally electrons have higher mobilities than holes so that n-type materials are preferred for good conductors. To have a good conductor, it is therefore interesting to have a material with a high electron density and a high mobility. However, free carriers are responsible for optical absorption so the electron density can not be too high, like in metals. When electrons interact with an oscillating electric field (light), they are excited and form a plasmon with a frequency given by the Drude's model:

$$\omega_p = \sqrt{\frac{ne^2}{m^*\varepsilon}} \tag{1.2}$$

where m^* is the effective mass of the electrons and ε is the permittivity of the material. The plasmon wavelength is given by $\lambda_p = 2\pi c/\omega_p$ and corresponds to the wavelength of incident photons that are absorbed due to the plasmons. Metals have a high electron density ($\gg 10^{22}$ cm⁻³) leading to a plasmon wavelength in the deep UV ($\lambda_p < 0.2 \ \mu$ m) and have medium mobilities. TCOs have intermediate electron densities ($n \sim 10^{21}$ cm⁻³), plasmon wavelengths in the near-infrared ($\lambda_p \sim 1 \ \mu$ m) and high mobilities. Polymer materials have low carrier densities ($n \sim 10^{20}$ cm⁻³), plasmon wavelengths in the mid-infrared ($\lambda_p > 1 \ \mu$ m) and low mobilities. [1] Metals have a very low resistivity but the plasmon energy in the UV induces high absorption and reflection in the visible spectrum. Polymers exhibit a low absorption but also a low conductivity that, for now, forbids their use in lots of TCEs applications. TCOs are currently the best compromise between a high optical transparency in the visibleinfrared range (>90%), and a low resistivity (< 10⁻⁴ Ω .cm). Their stability in time is also higher than for polymers, which is important for durable productions.

To obtain a good transparency in the visible and infra-red, the best strategy is to have a limited charge carrier density with the highest mobility. From this point of view, graphene is a very interesting material but it is still difficult to synthesize at large scale, contrary to TCOs that are industrially mature for several decades.

Comparison of TCEs: figure of merit

When TCEs are needed, the choice of the best material requires an objective comparison between the different available solutions. It is therefore interesting to define a quantity to characterize the performance of a material, called figure of merit. The optimal performances depend on the targeted application so it is not possible to define a universal figure of merit. For example, for large-scale applications the price is very important, while for specific applications such as spatial, the price is not limiting. Non-toxicity and bio-compatibility are also necessary in specific domains and not required in other devices. A common application of TCEs is solar panels. In this case, the main characteristics that have Other to be maximized are transparency and electrical conductivity. properties have to be considered such as the deposition temperature, the adhesion on the substrate, the deposition rate, the optical bandgap etc. but the requirements for these properties strongly depend on the type of solar cell, and not only on the TCE. For this reason, the figure of merit used for TCEs often only take the transparency and conductivity into account. Different figures of merit have been proposed that always increase with an increasing transparency (T) and a decreasing sheet resistance (R_s) . Typically, the figure of merit is composed of an increasing function of T divided by an increasing function of R_s and the type of function chosen depends on the importance to each parameter. For example, the Haacke's figure of merit is defined as: [13, 14]

$$\phi = T^{10}/R_s$$

The inconvenient of this definition is that it is related to a specific layer, not to a material, so it can be difficult to compare from different sources. Indeed, the sheet resistance is directly dependent on the thickness of a film, meaning that exactly the same material leads to significantly different figures of merit when the thickness is varied. Using the resistivity (ρ) is therefore scientifically more interesting since it is a material's property. The sheet resistance can however be interesting when a multi-layer TCE is used because R_s includes the resistivity of all the involved materials.

The use of the transmission is also unclear and leads to difficulties to compare different TCEs. Indeed the transmission depends strongly on the wavelength, due to the dependence of the absorption coefficient α on the wavelength, but also due to the interference that are present in thin films. The transmission and the interference also depend on the thickness, which makes it difficult to compare different materials from the literature. There are different possibilities to limit the inaccuracy due to the dependence of the figure of merit on the thickness and wavelength. First, it is possible to always take the transmission at the same wavelength. The problem is that depending on the thickness of the thin film, the wavelength can correspond to a reflection or transmission peak, for a same material. Another possibility is therefore to calculate the figure of merit at the wavelength with maximum transmission (minimum reflection) [15]. It is also possible to take the average transmission in a range. However, the adequate range depends on the targeted application. In general, as for the sheet resistance, the problem with the transmission is that it is not a property of a material and depends on the thickness, on the roughness of the layer and the substrate, on the material used as substrate, etc. Using the absorption coefficient is therefore more reliable to compare different materials. Gordon [16] proposed the following figure of merit using :

$$\phi = \frac{\sigma}{\alpha}$$

$$\phi = \frac{1}{R_s t} \frac{t}{\ln\left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right]} \simeq \frac{1}{R_s \ln\left(\frac{1}{T_{\text{max}}}\right)}$$
(1.3)

with σ the electric conductivity and t the thickness of the film, and

T and R the transmission and reflection, respectively. If the figure of merit is taken at a maximum of transmission T_{max} , it can be assumed that $R \simeq 0$. Cao *et al.* (Ref. [17]) realized a review of different types of TCEs available, with their respective sheet resistance and transparency (see Fig. 1.1. We superimposed the figure of merit ϕ as defined in eq. 1.3, assuming that $R \simeq 0$. With this comparison of different TCEs, we can see that the best figure of merit is obtained for metal grids or nanowires, TCOs and graphene. This value of figure of merit must however be taken with care. Indeed, graphene reaches good values even with high sheet resistance because $\phi \to \infty$ when $T \to 1$ when in reality there is little to no benefit in most applications to go from a transparency of 0.95 to 1. Another factor to take into account is that the transparency is actually an average transparency. Therefore, metal grids and TCOs have similar average transparencies even if the metal grids are actually a combination of transparent and opaque surfaces. While it is suitable for photovoltaics, it is not acceptable for applications such as touchscreens when an homogeneous surface is required.

In the TCEs market, TCOs are therefore by far the most common materials because of their high transparency, conductivity, hardness and durability. ITO is generally used in flat panels because it is still considered as the TCO with the best properties. However, for solar cells, ZnO:X and SnO₂:X are often preferred due to their lower cost. ZnO is often doped with aluminum (AZO), leading to slightly better properties (lower resistivity) than SnO₂. An other advantage of AZO over ITO, is its non-toxicity and abundance of source materials. These are the reasons why this thesis studies the properties of ZnO and AZO.

Deposition of ZnO and AZO

A common deposition technique of thin films in the industry is sputtering. This technique allows to deposit thin films with reasonably high deposition rate, of good quality and uniformity, at low temperature on various substrates. It was here studied in reactive mode to be able to change the stoichiometry since oxygen partial pressure during this process has been proven to be of primal importance. Because sputtering is a



Figure 1.1: State of the art of different TCEs available, taken from Cao et al. (Ref. [17]). We superimposed the curves of constant figure of merit, assuming that $R \simeq 0$.

deposition technique with out of equilibrium conditions, thermal energy of the particles is also a parameter of utmost importance. Therefore, the effect of temperature has also been studied during deposition, and during post-deposition annealings. The main difficulty with reactive sputtering is its inherent difficulty to control because it consists in the competition between several phenomenon that are very sensitive to the process parameters. For this reason it is possible to find many studies in the literature that present contradictory results because not all the parameters are well controlled, and some important technical information are lacking. In this thesis we tried to study the influence of the different parameters in a rigorous way, and understand their effect on the materials properties.

Structure of the thesis

This thesis is organized as follows :

- Chapter 2 introduces the theoretical back-ground necessary to understand this thesis, and makes a review of what can be done with ZnO/AZO.
- Chapter 3 introduces all the methods that have been used during this thesis to produce and analyze the thin films of ZnO and AZO. The focus was put on the understanding of the different strengths and limitations of the different techniques, to be aware of what can be understood with a technique and avoid drawing erroneous conclusions.
- Chapter 4 studies ZnO as a base material for AZO, to understand the effect of the micro-structure and the intrinsic defects on the opto-electro-mechanical properties. An innovative technique to study the micro-structure is the multi-beam optical stress sensor used in-situ during deposition. The minimum resistivity of intrinsic ZnO is too high to produce effective conductive electrodes, but the piezoresistance of the films has been studied and ZnO was proposed as a candidate for transparent piezoresistors.

- Chapter 5 studies the effect of aluminum doping of ZnO, to produce transparent electrodes with high transparency and conductivity. The focus is put on the type of defects, the deposition conditions that favor one type of defect or another and their effect on the electrical, optical and mechanical properties. This way recommendations can be done to reach the optimal deposition conditions regardless of the used equipment, which is of primal importance since the variability of the reported results in the literature is partly due to a lack of understanding of the effect of the different deposition parameters.
- Chapter 6 presents the lab-on-chip technique used at UCL to characterize the mechanical properties of free-standing thin films. This thesis focused on the optimization of this technique for brittle materials, and on the development of new fabrication processes to make it adapted to most materials such as metals, oxides, and 2D materials such as graphene, which could be the transparent electrode of the future.
- Chapter 7 concludes and analyses the future perspectives to continue this work on transparent electrodes and their mechanical testing, for AZO thin films and graphene.

Chapter 2

State of the art and theoretical background

Zinc oxide is a material that combines several interesting properties such as piezoelectricity, transparency, a direct bandgap and a high exciton binding energy. Depending on the doping levels, the electrical resistivity can vary from 10^{12} Ω .cm when undoped [18] to 10^{-4} Ω .cm when doped with aluminum [8], showing an exceptional range of resistivities while remaining transparent. ZnO thin films can be deposited by various techniques such as chemical vapor deposition (CVD) [19], e-beam evaporation [20], pulsed laser deposition [21] or sputtering [22]. An advantage of sputtering is that it can be used on almost any substrate because the deposition can be done at room temperature. There are two different modes in sputtering: reactive (Zn target in an Ar/O_2 plasma) or non-reactive (ZnO target in an Ar plasma). The advantage of the reactive mode is that the stoichiometry can be varied from pure Zn to stoichiometric ZnO by changing the oxygen concentration in the plasma, going through all the intermediate compositions. It means that depending on the oxygen concentration, the optical and electrical properties can be changed from a metallic to an insulating and transparent material.

This chapter introduces the theoretical background necessary to understand the processes described in the following chapters. It also reviews the state of the art of the understanding of the different possible defects in ZnO and their influence on the electrical properties of the thin films.

2.1 General properties

ZnO has a melting point of 1975°C but sublimation occurs at lower temperature if the oxygen partial pressure is low. [23] In reactive sputtering, zinc is sputtered and oxidized, on the target, on the substrate, or during the travel between those two. If the substrate is heated, re-evaporation of zinc atoms is non negligible given its high vapor pressure: [24]

$$\log(p_{\rm vap}) = 9.108 - 6776/T \tag{2.1}$$

where p_{vap} is the vapor pressure of Zn in mbar, and T is the temperature in K. The evaluation of this expression is plotted in Fig. 2.1. Other general properties of bulk ZnO are listed in table 2.1.

Structural properties

ZnO has a wurtzite structure (space group P6₃mc [25]) with lattice constants a = 3.253 Å, c = 5.213 Å and a theoretical value of c/a = 1.633. These values can be slightly modified by a deformation of the lattice due to stress or defects such as intersitial atoms, vacancies, dislocations or grain boundaries. [26] In the wurtzite structure, all atoms are tetragonally bonded with four neighbors in a sp³ covalent bonding with a substantial ionic character. The wurtzite structure can be seen as two interpenetrating hexagonal-close-packed sub-lattices of Zn and O atoms, shifted of 3c/8 along the *c*-axis. When the c/a ratio is changed, the angles between the atoms adapt to keep an almost constant distance between atoms. The zinc ions are substantially smaller (ionic radius of 0.74 Å) than the oxygen ions (ionic radius of 1.38 Å).

At high pressure (>9 GPa) a rock-salt structure is observed, resulting in a 16.7% decrease of the unit cell volume. [27] A zinc-blende structure (diamond cubic structure with alternating types of atoms at the different lattice sites) can also appear but is stable only by growth on cubic



Figure 2.1: Vapor pressure of zinc as a function of temperature. The horizontal line represents a typical pressure during sputtering.



Figure 2.2: Wurtzite structure observed in ZnO, with lattice constants a = 3.253 Å, c = 5.213 Å and a theoretical value of c/a = 1.633.

$E_g [eV]$	3.3					
Structure	Wurtzite					
Space group	$P6_3mc$					
a, c [Å]	3.25, 5.21					
Density $[g/cm^3]$	5.6					
$\kappa \; [\mathrm{W}.\mathrm{m}^-1.\mathrm{K}^-1]$	$69_{\parallel}, 60_{\perp}$					
$\alpha \ [10^{-6}/\mathrm{K}]$	$2.92_{\parallel}, 4.3_{\perp}$					
T_{melt} [°C]	1975					
$T_{melt,Zn}$ [°C]	420					

Table 2.1: General properties of bulk ZnO.

substrates such as ZnS. [28] These latter two structures were never observed in this work, hence only the wurtzite structure will be considered here and is presented in Fig. 2.2.

ZnO contains polar surfaces among which the most common are the positively charged Zn-(0001) and negatively charged O-(0001) surfaces. These charges result in a spontaneous polarization along the *c*-axis.

X-ray diffraction (XRD) is a widely used technique to characterize crystalline materials and a typical measurement obtained on ZnO powder is visible in Fig. 2.3. The position and intensity of the different peaks are shown in Table 2.2. In thin films deposited by sputtering (reactive and non-reactive), a strong texture is almost always observed with the *c*-axis oriented perpendicular to the substrate, resulting in XRD spectra where the (002) peak is largely dominant, [29–34] although the (103) peak is also commonly observed with a lower intensity. [35–38] In Ref. [35] they observed an increase of the (103) peak with temperature, for thin films of AZO deposited by confocal sputtering with ZnO and Al₂O₃ targets. An increase of the intensity of the diffraction peaks in AZO was also observed for annealings under nitrogen from 350 to 650°C. [39] However, the position of the peaks remained unchanged with the annealing.

With XRD spectra it is possible to evaluate the grain size of a material thanks to the Scherrer's formula (see eq. 3.2). Crystallite size from



Figure 2.3: XRD pattern of ZnO powder taken from the RRUFF project. [40]

2-θ	Ι	(hkl)
31.779	570	(100)
34.430	414	(002)
36.265	1000	(101)
47.554	210	(102)
56.615	301	(110)
62.876	264	(103)
66.4	40	(200)
67.971	214	(112)
69.112	105	(201)
72.587	16	(004)
76.988	32	(202)
81.411	16	(104)
89.646	65	(203)

Table 2.2: Position, relative intensity, and corresponding orientation of XRD peaks calculated for ZnO with wurtzite structure. PDF 089-0510

the literature for ZnO and AZO thin films deposited by sputtering are listed in Table 2.3. It can be observed that the grain size evaluated by Scherrer's formula is largely underestimated compared to what is observed by SEM or AFM. This is due to the fact that Scherrer's formula gives a lower bound to the grain size. This will be discussed with more details in section 3.1.

In Ref. [30], ZnO thin films were deposited with RF magnetron sputtering, with a ZnO target in an Ar + O_2 plasma. The effect of the oxygen partial pressure and the total pressure was analyzed through XRD. Total pressure had a higher effect on grain size (from 23 to 34 nm) than the oxygen partial pressure (25 to 29 nm). It is also possible to evaluate the stress in a thin film with XRD thanks to the variation of the lattice parameters. [41] For a thin film, the expression of the in-plane stress is:

$$\sigma = \left(C_{13} - C_{33}\frac{C_{11} + C_{12}}{2C_{13}}\right)\frac{c - c_0}{c_0} \tag{2.2}$$

The values of the stiffness constants for ZnO are $C_{11} = C_{33} = 210$ GPa, $C_{12} = 120$ GPa and $C_{13} = 105$ GPa, [42] leading to the following expression:

$$\sigma = 225 \frac{c_0 - c}{c_0} \text{ [GPa]}$$

The problem with this technique to evaluate the stress is that the variation of c due to stress is often small compared to the accuracy on c_0 , leading to high errors. Therefore, a shift of a peak should more be considered as a qualitative information of the variation of stress from one sample to another one. The limitations of this technique will be discussed in section 3.1.

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Note	No clear relation between thick-	ness and grain size			AFM shows grains of $\sim 100-300$	nm	AFM shows grains of $\sim 50 \text{ nm}$	ZnO target, Ar+O ₂ plasma at	different pressures	Grain size increases with oxyger	partial pressure	Grain size increases with oxyger	partial pressure	AFM shows grains of $\sim 50 \text{ nm}$	Confocal sputtering	$\sim 50 \text{ nm}$ grains observed by SEM	40-60 nm columns observed by	SEM
Material	$_{\rm ZnO}$		ZnO		ZnO		AZO	ZnO		ZnO		AZO		$_{\rm ZnO}$	AZO	ZnO	AZO	
t [nm]	220-400		100, 200,	400, 1300	1000		066	252 - 372		~ 600		~ 600		68-90	100	340 - 360	360-540	
T [°C]	I		65		150		150	RT°		<100-150		<100-150		RT°	20 - 100	RT°	RT°	
D [nm]	22-35		16, 17, 24, 80		26.4		13.6	23-34		20-53		19-37		32-38	15-18, 9-11	4-13	25-34	
Technique	RF-NR		RF-NR		RF-NR		RF-NR	RF-NR		DC-R		DC-R		RF-NR	RF-NR	RF-R	RF-NR	
Ref.	[29]		[31]		[32]		[32]	[30]		[33]		[33]		[34]	[35]	[36]	[37]	

2.1. General properties

Table 2.3: Grain size for ZnO and AZO thin films deposited by sputtering, evaluated by the Scherrer's formula based on the XRD spectra.

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Figure 2.4: Strucutral zone model developed by J.A. Thornton. Image adapted from Ref [43]. E_p denotes the energy of the incident particles.

For sputtering, the structural zone model developed by J.A. Thornton is well known for metallic films. [43] Some comparisons can however be done for oxide films deposited by reactive sputtering. Indeed the structure of a thin film is partly determined by the mobility of its species, depending on the homologous temperature (T/T_m) . For reactive sputtering in metallic and transition mode, since the metallic atoms are oxidized at the surface, the homologous temperature of the metal must be taken into account. For sputtering in the oxide mode, the homologous temperature of the oxide must be taken into account. This zone model is shown in figure 2.4. Zone 1 is composed of tapered crystallites separated by voids, zone T is composed of fibrous grains embedded in a void-free amorphous matrix, zone 2 is composed of columnar grains separated by dense inter-crystalline boundaries, and zone 3 is composed of recrystallized grains. [44]



Figure 2.5: Electronic band structure of ZnO calculated using the HSE hybrid functional. Taken from Ref. [45].

Electronic band structure

ZnO is a semi-conductor with a direct bandgap of ~ 3.3 eV (near-UV spectral region) at the Γ point of the Brillouin zone as can be seen in the electronic band structure in Fig. 2.5. This band structure is valid for bulk ZnO. In real polycrystalline ZnO, surface states are present as well as impurities levels. The higher curvature of the conduction band than the valence band indicates a lower effective mass, hence higher mobility, for electrons than for holes.

2.2 Applications of zinc oxide

Zinc oxide is a material that has been studied for several decades because of its numerous interesting properties such as piezoelectricity, a high exciton binding energy, a wide direct bandgap, transparency to visible and near infrared light, and the ability to be highly doped while remaining transparent. Many applications are possible for ZnO thin films, but two that are of particular interest for doped zinc oxide are transparent electrodes and transparent transistors.

2.2.1 Transparent electrodes

In solar cells, a p-n junction generates current when exposed to light. To collect the current, electrodes must be placed on both sides of the solar panel. The back electrode can be made of a conductive material that is not transparent. The front electrode however lays between the light source and the p-n junction so if it is made of a continuous metal layer, no light can reach the absorber and no current is generated. One solution is to use a metal grid to collect the current, but this metal partially reflects light, hence reduces the generated current. Using larger grids reduces this problem but increases the losses because the charge carrier have a longer distance to travel before reaching the contacts. Another possibility is to use transparent conductive materials (TCO) to collect the current while transmitting the light at the same time. The material with the best properties at the moment is indium tin oxide (ITO), a mixture of about 90% indium oxide (In_2O_3) and 10% tin oxide (SnO₂). [46] The resistivity can go down under 10^{-4} Ω .cm with a high transmittance (above 90%). [47, 48]

Another application of transparent electrodes is the display technology, for example in LCD screens where the liquid crystals must be oriented with the application of an electric field. [49] TCO such as ITO are also used in OLED as an anodic material to facilitate hole injection while letting the light escaping the device. [50, 51] Some satisfactory results were also obtained on AZO to obtain indium-free OLEDs. [52, 53].

2.2.2 Transparent transistors

For transparent transistors, an advantage of ZnO is its good crystalline quality in thin films, even when deposited at room temperature. Therefore, relatively high electronic mobilities (10-50 cm²/Vs) can be obtained for charge carrier densities below 10^{19} cm⁻³, much higher than in amorphous silicon (~ 1 cm²/Vs). [23] Organic semi-conductors can also be synthesized at low temperature but have lower mobilities and a lower stability. Thanks to its wide bandgap, ZnO is fully transparent to visible light, and its behavior is less light sensitive. [54] Numerous articles report ZnO-based transparent transistors with ON/OFF ratio up to 10^8 . [34, 35, 55–59]

2.3 Electrical properties

The study of electrical properties of ZnO started several decades ago, especially on sintered polycrystalline samples. A review of these early observations was made in 1959 by Heiland et al. [60] A problem of these samples is that they were often porous, inhomogeneous and with a density lower than bulk ZnO. [23] Single crystals of a few milimeters were already synthesized in the 1950s by chemical vapor transport [61, 62] and hydrothermal growth. [63]

2.3.1 Defects in intrinsic ZnO

Polycrystalline materials contain many defects, but even single crystals contain defects that can act as dopants, or influence the mobility of the charge carriers. These intrinsic defects in ZnO are typically zinc interstitials and/or oxygen vacancies. Another type of defects that is often present in ZnO is hydrogen, creating unwanted doping.

In general, a lot more defects than the previous three are possible in ZnO. Zn and O can both form vacancies or interstitials, denoted V_{Zn} , Zn_i, V_O , and O_i respectively. Antisites (O in Zn position and inversely) are also possible, but vacancies and interstitials can carry a charge of ± 2 while antisites can carry a charge of ± 4 . This makes vacancies and interstitials more likely than antisites in polar compounds. [23] There can also be combinations of these defects such as Frenkel pairs, where a cation leaves its site in the lattice creating a vacancy, and becomes interstitial nearby its initial position. Schottky pairs are formed by a Zn vacancy accompanied by an O vacancy. The Frenkel and Schottky pairs are thus neutral defects.

Ab-initio simulations have been performed to evaluate the formation energy of each defect to estimate which are the more likely to form. The defect concentration is estimated by:

$$c = N \exp\left(-\frac{\Delta H_f}{k_{\rm B}T}\right) \tag{2.4}$$

with c the equilibrium concentration of defects in the crystal, ΔH_f the formation enthalpy of a defect, and N the concentration of sites in the crystal where the defect can occur. The result of the calculation depends on the hypotheses considered, depending on the growth conditions. It can be zinc-rich ($\mu_{Zn} = \mu_{Zn,bulk}$) or oxygen-rich ($\mu_O = \mu_{O_2}$). [26] It is important to note that the formation energy strongly depends on the chemical potential of the species and on the Fermi level (chemical potential of electrons and holes). [64] The dependence of the formation energy on the Fermi level is depicted in Fig. 2.6 for the zinc-rich and oxygen-rich conditions, two extreme cases of the chemical potentials. Intermediate situations can be obtained for different chemical potentials. For example, the chemical potential of a gas (oxygen in this case) is related to its partial pressure. The higher the partial pressure of oxygen during sputtering, the closer to the oxygen-rich situation the system will be. From Fig. 2.6, we can deduce that an increase of the oxygen partial pressure will thus favor (decrease of ΔH_f) the incorporation of interstitial oxygen (O_i) and the creation of zinc vacancies (V_{Zn}) . The slope of the curves in Fig. 2.6 depends on the charge state of the defects. A donor-like defect like Zn_i can be neutral, have a charge of +1, or +2 depending on the position of the Fermi level. If the Fermi level is higher than the defect level, the donor is not ionized (neutral charge) and the formation energy does not depend on the position of the Fermi level. If the Fermi level decreases under the donor level $(E_F < E_D)$, an (two) electron(s) from the donor is (are) transferred to the electron gas, accompanied with an energy gain $\delta = q(E_D - E_F)$ per electron released. It means that when the Fermi level is decreased, donor defects (Zn_i, V_O) become more stables and acceptor defects (V_{Zn}, O_i) become less stable. Based on this study, under zinc-rich conditions the most stable defect is oxygen vacancy, while under oxygen-rich conditions both oxygen interstitial and zinc vacancy are possible, depending if the Fermi level is low or high, respectively. Note that a frequent problem with GGA is the under-estimation of the band-gap, as observed here. The difference between the simulated and experimental bandgaps is represented with the shaded grey area. In Fig. 2.6, the subscripts $_{oct}$ and $_{db}$ represent octahedral and dumbbell respectively, two possible interstitial configurations. The dumbbell interstitial is more stable, and can act as donor and acceptor (amphoteric defect) but is a deep level in both situations, meaning that it does not contribute to the electrical conductivity. However, it is of primal importance to describe the oxygen diffusion in ZnO.

A very important concept that can be observed in Fig. 2.6 is selfcompensation. [66, 67] When donors are introduced the Fermi level increases and intrinsic acceptors become more stables (lower formation enthalpy), limiting the number of free electrons. The opposite phenomenon is at the origin of the difficulty to obtain p-type ZnO. When acceptor atoms are introduced in ZnO, the intrinsic donor defects become more stable and compensate the dopants.

2.3.2 Scattering of charge carriers in single crystals

Even in an hypothetical perfect single crystal, the mobility of electrons would not be infinite due to interactions with the lattice and defects. [68] At room temperature an important source of scattering is phonons. A phonon is a quasi-particle representing a quantum of vibrational energy in a lattice of atoms oscillating at a single frequency. There are two categories of phonons: acoustic and optical. The acoustic phonons are a coherent movement of the atoms and the optical phonons correspond to an out-of-phase movement of neighbor atoms. In real crystals, impurities are also present and cause scattering of the charge carriers. For single crystals of ZnO, the maximum mobilities reported at room temperature is in the range $\mu_n = 200 - 225 \text{ cm}^2/\text{Vs}$. This is significantly smaller than other semi-conductors ($\mu_n[\text{Si}]=1415 \text{ cm}^2/\text{Vs}$, $\mu_n[\text{GaAs}]=8500 \text{ cm}^2/\text{Vs}$) because of the strong polar optical scattering in ZnO. Following the review of Klein et al. [23], the scattering processes in single crystals can be grouped in the following categories.



Figure 2.6: Variation of defect formation enthalpies with Fermi level under zinc- (left) and oxygen-rich (right) conditions obtained from generalized gradient approximations (GGA)+U calculations. The gray shaded area indicates the difference between the calculated and the experimental band gap. The numbers in the plot indicate the defect charge state. Parallel lines imply equal charge states. Donor defects are indicated in blue and acceptor in red. Amphoteric defects are drawn in black. Taken from Ref. [65].

Optical scattering

The origin of this scattering is the interaction of electrons with the electric field induced by the lattice vibration polarization that occurs in partially ionic semiconductors. Devlin [69] calculated the optical Hall mobility with:

$$\mu_{H_{opt}} = r_{H_{opt}} \phi \frac{e}{2\alpha\omega_0 m^*} \left[\exp\left(\frac{\hbar\omega_0}{k_B T}\right) - 1 \right]$$
(2.5)

where α is the polaron coupling constant given by:

$$\alpha = \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_s}\right) \sqrt{\frac{m^* E_H}{m_e \hbar \omega_0}} \tag{2.6}$$

 $r_{H_{opt}}\varphi$ is usually assumed as equal to 1, m^* and m_e are the effective and vacuum masses of electrons, $\hbar\omega_0$ is the energy of the longitudinal optical phonon (73.1 meV), E_H is the first ionization energy of the hydrogen atom (13.6 eV), ε_{∞} and ε_s are the high frequency and static dielectric constants.

Acoustical scattering

It is well known that a strain can slightly change the band structure of a material. Acoustic phonons cause a local strain, hence shifts the band edges and modifies the mobility of the charge carriers. The acoustical lattice mode Hall mobility has been calculated by Bardeen and Shockley: [70]

$$\mu_{H_{ac}} = r_{H_{ac}} \frac{\hbar^4 c_l e}{3E_1^2} \sqrt{\frac{8\pi}{m^{*5} (k_B T)^3}}$$
(2.7)

where $r_{H_{ac}} = 3\pi/8$ is the Hall coefficient for acoustic phonon scattering, c_l is the average longitudinal elastic constant and E_1 is the energy shift of the conduction band per unit deformation. E_1 is not well known for ZnO but it does not have a large importance for the overall properties because optical and piezoelectric scattering are dominant in ZnO. [68]

Piezoelectric scattering

As previously said, acoustical phonon cause a local strain of the crystal. If the crystal does not have an inversion symmetry, this strain creates a local electric field that scatters charge carriers. The piezoelectrically limited mobility was calculated by Zook: [71]

$$\mu_{H_{pie}} = r_{H_{pie}} \frac{16\sqrt{2\pi}h^2\varepsilon}{3eP_{\perp,\parallel}^2\sqrt{m^{*3}k_BT}}$$
(2.8)

where $r_{H_{pie}} = 45\pi/128$ is the Hall coefficient for piezoelectric mode scattering, $P_{\perp,\parallel}$ represents the average piezoelectric electro-mechanical coupling coefficients, perpendicular and parallel to the c-axis (0.21 and 0.36 respectively [68]). This anisotropy leads to an anisotropic electronic mobility, with $\mu_{\perp}/\mu_{\parallel} = 2.8$ [71] or 2.94 [68]. However, piezoelectric scattering is significant only at low temperatures (~100 K), so that the room-temperature mobility is isotropic. [72] All scattering processes have different temperature dependences and the one that limits the mobility at room temperature in undoped single crystals is the polar optical scattering.

lonized impurity scattering

Electronic mobility is also limited by the scattering due to the screened Coulomb potential of charged impurities. For non-degenerate semiconductors such as intrinsic ZnO, the ionized impurity mobility was calculated by Chattopadhyay and Queisser (valid up to carrier concentrations of about 5×10^{18} cm⁻³): [73]

$$\mu_{H_{ii}} = r_{H_{ii}} \sqrt{\frac{2\pi}{m^*}} \frac{128\varepsilon^2 (k_B T)^{3/2}}{N_i Z^2 e^3 \ln\left(\frac{24m^*\varepsilon (k_B T)^2}{n(e\hbar)^2}\right)}$$
(2.9)

where $r_{H_{ii}} = 315\pi/512$ is the Hall coefficient for ionized impurity scattering, n and N_i are the charge carrier and impurity concentration respectively. For high charge carrier concentrations, Shockley proposed another expression: [74]

$$\mu_{ii}^{sh} = \frac{3\varepsilon^2 h^3}{Z^2 m^{*2} e^3} \left(\ln\left[1 + \left(\frac{3^{2/3} \pi^{1/3} \varepsilon h^2 n^{1/3}}{2m^* e^2}\right)^2 \right] \right)^{-1}$$
(2.10)

Neutral impurity scattering

Neutral impurity can also scatter charge carrier. However in ZnO the shallow donors such as Al have a low ionization energy (around 50 meV), leading to a very low concentration of neutral donors at room temperature because the ionization energy is even further reduced in a semiconductor that is degenerately doped. [23] This scattering process can therefore be neglected.

2.3.3 Scattering in thin films

For transparent electrodes applications, the deposition techniques (such as sputtering) lead to polycrystalline thin films with lots of defects such as grain boundaries and dislocations. Both these defects have a strong impact on the electric properties of ZnO thin films

Dislocation scattering

Dislocation density in ZnO thin films can be very high, on the order of 10^{12} cm⁻², corresponding to an average distance of about 10 nm. [75] These dislocations contain defects (around 10^7 cm⁻¹) that can be charged and scatter the carriers. Stacking faults are also present due to the precipitation of interstitial zinc accompanied by the formation of oxygen vacancies. Since oxygen vacancies have a charge of Z = 2, their scattering power is higher than that of single ionized dopants such as Al. [23]

Grain boundaries

The ZnO thin films deposited during this thesis typically have columnar grains with a diameter of a few tens of nanometers, leading to a large grain boundaries density. These grain boundaries induce local perturbations in the crystallographic arrangement and create defects in the band gap of the semi-conductor. The grain boundaries can also act as electron traps, creating a depletion zone on both sides of the grain, accompanied by a barrier height ϕ_B for the electrons. Seto [76] developed a model to describe electronic transport in polycrystalline silicon. He assumed that electron trap states form a δ - shaped density of state in the band gap that are completely filled. The Seto's model leads to an effective mobility (μ_{eff}) dominated by thermionic emission across the grain boundaries:

$$\mu_{eff} = \mu_0 \exp\left(-\frac{\phi_B}{k_B T}\right) \tag{2.11}$$

where μ_0 is the mobility inside the grain given by: [76]

$$\mu_0 = \frac{eL}{\sqrt{2\pi m^* k_B T}} \tag{2.12}$$

with L being the grain size.

Two different regimes are observed in the variation of the barrier height. First, when the amount of free charges available in the grains is lower than the charge carrier trap density N_t , the grains are completely depleted and the traps are partially filled (case for $Ln < N_t$, with *n* the charge carrier density in the bulk). In this situation, an increase of the charge carrier density fills the traps and increases the barrier height:

$$\phi_B = \frac{eL^2n}{8\varepsilon} \ [eV] \tag{2.13}$$

Second, when $Ln > N_t$, the traps are completely filled and the grains are only partially depleted. In this situation, the depletion length decreases when the charge carrier increases, and the barrier height decreases: [76]

$$\phi_B = \frac{eN_t^2}{8\varepsilon n} \ [eV] \tag{2.14}$$

For a grain size of 30 nm and a trap density of $5 \cdot 10^{12} \text{ cm}^{-2}$ the maximum barrier height is 0.4 eV when $n = 1.7 \cdot 10^{18}$. Common charge carrier densities in AZO are around 10^{20} cm^{-3} , leading to barrier height inferior to 0.01 eV. In this situation (high electron density), the barrier width is very narrow and tunneling through the barriers takes place in addition to the thermionic emission discussed previously. Experimentally, the observed mobilities in thin films are lower than the one predicted by this model because there is an additional scattering due to defects such as point defects or dislocations.

In a semi-conductor with a high electron density, the depletion width is very narrow, enabling quantum-mechanical tunneling of the barriers by electrons.

2.4 Light transmission

In general, ZnO is transparent in the whole visible spectrum, from its band-gap (~ 3.2 eV or 380 nm) to near-infrared (~ 1.2 eV or 1000 nm). [29,77–79], Non-stoichiometric ZnO_{x<1} however can be absorbent in the visible region. These absorbent films can be obtained when the source material is zinc and the oxidation is not complete, like in reactive sputtering with a low oxygen concentration (see Chap. 4). It can also be obtained when the thin films are deposited with a ZnO source that is reduced during the deposition process. It can be observed in thermal evaporation [80, 81], or slightly in sputtering when a plasma of pure argon is used. To counter the observed reduction during non-reactive sputtering, small amounts of oxygen can be added to obtain stoichiometric ZnO, even if a stoichiometric target is used. For energies higher than the optical bandgap, the absorption coefficient is always high but an annealing can improve the quality of the film and increase the absorption coefficient furthermore. [82]

Doping usually does not significantly increase the absorption in the visible range as long as the film is completely oxidized, for aluminum [83], boron [84,85] or gallium doping [86]. It can however increase the transmission in the near-UV by increasing the optical bandgap through the Burstein-Moss effect if the charge carrier density increases. The maximum obtained bandgap for AZO is usually lower than 3.8 eV. [87]

In the infrared, the absorption increases with the charge carrier concentration due to plasmons, as discussed in the introduction, and as it will be observed in Chap. 5.

2.5 Deposition techniques

Different deposition techniques are available to obtain ZnO thin films, such as sputtering, chemical vapor deposition (CVD), pulsed laser deposition (PLD), or thermal evaporation. As previously said, thermal evaporation leads to under-stoichiometric films with a lower transmission in the visible spectrum. PLD gives films of good quality but CVD and sputtering are of particular interest because they are used industrially.

PLD uses a laser to ablate a target and deposit the material on a substrate placed in front. As in sputtering, an advantage of PLD is that a film with a complex stoichiometry can be deposited if a target with the desired composition is used. An other advantage is that the energy is brought by a laser that does not require any gas, unlike sputtering. This means that if reactive deposition is used, the gas pressure and composition can be varied independently of the stability of the process. The main disadvantage of this technique is the difficulty to obtain homogeneous samples on large substrates, which is why it is not commonly used in industrial process. Very low resistivity $(8.5 \times 10^{-5} \ \Omega \cdot \text{cm} \ [8])$ can however be obtained for AZO.

Sputtering is commonly used to deposit ZnO and AZO thin films and the process will be detailed in Chap. 4 and 5 for the reactive sputtering. The lowest obtained resistivities for AZO are slightly higher than for PLD, generally between 2 and $5 \times 10^{-4} \ \Omega \cdot \text{cm}$. [88–92]

CVD is commonly used in industrial applications. An advantage of this technique for ZnO thin films used in solar cells is that rough films can be obtained as deposited. The roughness is here desirable because
it scatters light, hence improves the light trapping and the produced current when AZO is used as front electrode in solar panels. [93, 94] Films deposited by sputtering often have a much smaller roughness and a supplementary etching step is required to obtain the desired roughness. CVD however generally leads to optimal electrical and optical properties at higher temperatures ($\sim 400^{\circ}$ C for AP-CVD and $\sim 160^{\circ}$ C for LPCVD [23]) than for sputtering, where room temperature deposition is possible.

2.6 Mechanical properties

ZnO is a brittle material with a linear elastic behavior as most oxides. Common values of the elastic modulus and the hardness of ZnO thin films are 110 and 9 GPa respectively, however values have been reported over a wide range. For epitaxial ZnO thin films grown on sapphire, a higher elastic modulus (154 GPa) was observed by Navamathavan et al. [95] and is attributed to compressive stress due to the lattice mismatch between the film and the substrate. For ZnO thin films deposited by sputtering on a silicon substrate, Fang et al. [96] observed an increase of the intensity of the (002) peak in XRD and an increase of the hardness (from 4 to 6 GPa) and elastic modulus (from 61 to 125 GPa) when the sputtering power is varied from 150 to 225 W. The enhancement of the mechanical properties is associated to a higher quality crystalline structure.

Chang et al. [97] observed for AZO thin films deposited by sputtering that when the deposition temperature is increased, the elastic modulus does not seem to be affected, while the hardness increases from 8 to 10 GPa when the temperature is varied from room temperature to 200°C. Kar et al. [98] observed a decrease of the elastic modulus and hardness when the sputtering pressure is increased from 3 to 15 mTorr. This is due to the fact that a lower pressure induces denser films. At the lowest pressure (1 mTorr) however, a deterioration of the mechanical properties was observed and is attributed to high energy particles bombardment. The highest elastic modulus and hardness coincided with the highest electronic mobility and density, and is attributed to an improved crystallinity. The fracture strain of ZnO and AZO films have been evaluated by bending of thin films deposited on polymer substrates. Sierros et al. [99] observed a fracture strain comprised between 0.3 and 2% depending on the thickness of the thin film (varied between 100 and 1100 nm). They attribute the variation of fracture strain to a stress gradient that changes the average stress between tensile and compressive. The films deposited with the highest compression have the highest fracture strain. Other studies found similar values of fracture strain between 0.5 and 1%. [100, 101]

Chapter 3

Materials and methods

This chapter describes the main techniques and equipments used during this thesis, and the principles necessary to have a critical point of view of the obtained results. The first section focuses on X-Ray diffraction, introducing the information that it can provide, and the limits of the technique that can lead to false interpretation of the results. Spectrophotometry is then introduced and the extraction of the optical properties of thin films is then described. An important point of this thesis is the analysis of the internal stress during growth, that is here measured with a multi-beam optical stress sensor (MOSS). The basics of sputtering are then introduced. It only explains the general principles of sputtering and deeper explanations can be found in Chap 4 and 5. The equipments and technique used for electrical characterization of the thin films are then presented. Finally, for the mechanical characterization of the thin films, the lab-on-chip technique has been used during this thesis and is discussed in details in Chap. 6. As it will be discussed, the release needed in this technique is the most critical step and XeF_2 has been selected as the most promising way to obtain reliable results but is still not mature enough. This XeF_2 release is therefore detailed at the end of this chapter.

3.1 X-Ray Diffraction (XRD)

X-Ray diffraction is used to characterize the crystallography of a sample. Indeed, regularly arranged atoms diffract light in preferential directions and each crystallographic structure has a specific diffraction pattern that can be identified. The condition for light to be diffracted is that the wavelength must be comparable to, or less than the interatomic distance. Such wavelengths correspond to X-Rays. In this work, the X-Rays used correspond to the $K_{\alpha 1}$ emission peak of copper, with a wavelength $\lambda_{CuK_{\alpha 1}} = 0.15418$ nm.

The origin of these diffraction peaks has been explained by Bragg. When the incident wave reaches a material, it is partially and specularly reflected by the parallel atomic planes of the crystal. The reflected waves interfere with each other and lead to a peak of intensity when the interference is constructive. The condition for the constructive interference to occur is that the difference of optical path lengths between waves reflected on different atomic planes is equal to an integer multiple of the wavelength. This situation is represented in Fig. 3.1 and leads to the Bragg's law which describes the angles of incidence that correspond to constructive interference:

$$2d\sin\theta = n\lambda\tag{3.1}$$

To obtain a diffraction spot the incident angle must verify the Bragg's law for a family of atomic plane existing in the analyzed material. To observe this peak, an additional condition is that the normal of the diffracting plane must be the bisector of the angle defined by the source, the incident spot and the detector (crystal orientation condition). To observe the peaks of all atomic planes present in the material a scan is performed for different angles since the wavelength is fixed. In a material without texture there are crystallites in every orientations. When the incidence angle corresponds to an atomic plane that verifies the Bragg's law, there are always crystallites with the right orientation so that the diffracted spot can be observed. In a textured material, some crystallite orientations are preferred over others. In ZnO deposited by sputtering, the main orientation is with the c-axis oriented perpendicularly to the



Figure 3.1: Representation of the conditions to obtain constructive interference in X-Rays Diffraction (XRD). The difference of optical paths between the two waves is equal to $2d\sin\theta$.

substrate. If all the crystals have this orientation, only the (002) peak can therefore be observed due to the orientation condition.

XRD can also give other information such as an evaluation of the grain size thanks to the Scherrer's formula.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{3.2}$$

with λ the wavelength ($\lambda_{CuK_{\alpha 1}} = 0.15418 \text{ nm}$), θ the diffraction angle and β the full width at half maximum (FWHM) in radian. The origin of this formula is that in grain boundaries there are defects that locally strain the crystal (tensile and compressive). This strain locally changes the distance between the atomic planes, hence the angle verifying the Bragg's law, inducing a broadening of the peak. The smaller the grains, the more there are grain boundaries, the larger the broadening. However, other defects such as dislocations, stacking faults, chemical heterogeneities also induce a peak broadening. Therefore, the Scherrer's formula that only takes the grain boundaries into account, gives only a lower bound on the grain size. [102]

It is also possible to evaluate the stress in a thin film with XRD. Indeed, the position of the peaks is directly related to the lattice parameters. With the (002) peak we can calculate the *c* parameter thanks to the Bragg's law (equation 3.1), hence the strain along the *c*-axis perpendicular to the substrate : $\varepsilon_z = (c - c_0)/c_0$. From this strain, it is possible to calculate the stress. In general, the stress σ is given by :

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{12} & C_{22} & C_{13} \\ C_{13} & C_{13} & C_{33} \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \end{bmatrix}$$
(3.3)

where C_{ij} are the elastic stiffness constants and ε is the elastic strain. [41] The stress perpendicular to the substrate is zero due to the free surface, hence

$$\varepsilon_x + \varepsilon_y = -C_{33}\varepsilon_{zz}/C_{13} \tag{3.4}$$

The in-plane stress shows no preferred orientation meaning that

$$\sigma = \frac{\sigma_x + \sigma_y}{2} = \frac{(C_{11} + C_{12}) * (\varepsilon_x + \varepsilon_y) + 2C_{13}\varepsilon_z}{2}$$
$$\sigma = \left(C_{13} - C_{33}\frac{C_{11} + C_{12}}{2C_{13}}\right)\frac{c - c_0}{c_0}$$
(3.5)

The values of the stiffness constants for ZnO are $C_{11} = C_{33} = 210$ GPa, $C_{12} = 120$ GPa and $C_{13} = 105$ GPa. [42] When these values are introduced in equation 3.5, it gives the following relation :

$$\sigma = 225 \frac{c_0 - c}{c_0} \text{ [GPa]}$$
(3.6)

This method however has a low accuracy, typically of several hundreds of MPa due to the imprecision on the value of c and c_0 . [103]

For thin films, especially when they are highly textured, the position of the sample is very important to observe the diffraction peaks (orientation condition). The equipment used for this thesis is usually used for bulk materials or powders, where the results are less sensitive to the position. To evaluate the possible mistake on the measured values, experiments were done on textured thin films (ZnO) and mono-crystalline silicon substrates. These results are shown in Fig. 3.2.

The first experiment was to induce an initial tilt between the θ and 2θ angles, to simulate the effect of a tilt of the sample. The analyzed

peak is here the (100) peak of the silicon substrate. It can be seen that the intensity is increased by three orders of magnitude (~ 35 to 39 000) when the initial tilt goes from 0 to -0.75°. It is then almost stable (still 20% variation) for a range of 0.75°, before dropping again by several orders of magnitude. The different scans that have been run during this thesis have shown that the angle of the sample cannot be controlled with enough accuracy to obtain repeatable results on highly textured samples. Note that this high sensibility is due to the perfect texture of the silicon substrate. The results for ZnO are also sensitive due to their (002) texture, but not as much as silicon substrates. No shift of the peak is observed however.

The second studied parameter was the influence of the position in z of the sample. It has been varied over 1 mm, and the main influence is a shift of the peak of about 0.4° . The intensity of the peak varied of about 17%, which is much smaller than with the tilt variation, but not negligible. With our setup the accuracy of the z-positioning can be considered as 0.02 mm, leading to an imprecision on the position of 0.008° and 0.3% of the intensity. This parameter should therefore be a negligible source of imprecision in our experiments.



Figure 3.2: XRD spectra taken with different initial tilt of the sample, from -3° to $+3^{\circ}$ (Top) and for different initial positions in z, from 2.5 to 3.4 mm (Bottom).

3.2 Spectrophotometry

Spectrophotometry is the measurement of the transmission and/or reflection of material as a function of the wavelength. The equipment used in this thesis is a Specord 200 PLUS from Analytic Jena, for wavelengths between 300 and 1100 nm with a 1 nm resolution. The sample holder for the reflection required larger samples so it could only be recorded for the ZnO samples and not the AZO samples (see Chap. 5 for details). The principle of this technique is to measure the transmission (T) and the reflection (R) to obtain the absorbance (A) of the sample (A = 1 - T - R). The absorption of the sample can then be related to its electronic properties such as the band gap. Indeed, when a photon has an energy sufficient to excite an electron from the valence to the conduction band, it will be absorbed. If its energy is not sufficient to activate this transition, it will not be absorbed and the sample is transparent. In the infrared range, different absorption mechanisms occur and the absorption is increased with the free charge carrier density. Based on the transition between absorbent to transparent, the optical bandgap can be deduced thanks to the empirical Tauc's relation that describes the evolution of the absorption with energy:

$$(\alpha h\nu)^{1/n} = K(h\nu - E_g)$$
 (3.7)

where α is the absorption coefficient, h is the Plank's constant, ν is the photon frequency, K is a proportionality constant, E_g is the optical bandgap corresponding to the difference between the bottom of the conduction band and the top of the valance band, or between the Fermi level and the top of the valance band in the case of a degenerate semiconductor. Indeed, to be absorbed by an electron of the top of the valence band, a photon needs an energy at least sufficient to excite the electron to the first allowed unoccupied state. This first unoccupied allowed state corresponds to the bottom of the conduction band for an intrinsic semi-conductor, and to the Fermi level in a degenerate semiconductor. The value of the exponent n depends on the nature of the electronic transition: [104]

• for direct allowed transitions: n = 1/2



Figure 3.3: Example of the application of the Tauc plot to extract the optical bandgap from the absorption coefficient.

- for direct forbidden transitions: n = 3/2
- for indirect allowed transitions: n = 2
- for indirect forbidden transitions: n = 3

In the case of ZnO and AZO, the absorption is due to a direct allowed transition so n = 1/2. It means that if $(\alpha h\nu)^2$ is plotted as a function of the energy $(h\nu)$, its value should be 0 when the energy equals the optical bandgap. In reality, the Tauc's relation is not valid when $h\nu < E_g$ because $(\alpha h\nu)^2$ cannot be negative. Close to the bandgap, the relation is not valid either because some defects create absorption states near the band edge. The transition between transparent to absorbent is therefore not perfect since real materials contain defects. At high energies, a saturation of available transition states leads to a saturation of the absorption coefficient. To obtain the optical bandgap, $(\alpha h\nu)^2$ must therefore be fitted in the range where a linear behavior is observed and extrapolated to lower energies. The intercept between the fit and the $h\nu$ -axis gives the optical band gap, as represented in Fig. 3.3. The absorption coefficient α must theoretically be calculated with the transmittance (T) and reflectance (R) with the formula: [105]

$$\alpha(\lambda) = \frac{1}{t} \ln\left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right]$$
(3.8)

where t is the thickness of the film. However, as said previously, the reflection could not be measured on the AZO samples for practical reasons. For transparent films on transparent substrates R is small so an approximated formula can be used with the hypothesis that $R \simeq 0$, without inducing a large error on the evaluation of the bandgap:

$$\alpha(\lambda) \simeq \frac{1}{t} \ln\left(\frac{1}{T}\right) \tag{3.9}$$

To estimate the error done with this formula, an approximation has been done for an AZO sample with a high transparency. In this case, a reasonable value for the reflectance would be 0.1. Therefore, for a film of 350 nm, using equation 3.9 instead of equation 3.8 would lead to an overestimation of $\alpha h\nu$ of $\sim 5.5 \cdot 10^5$ eV/m. In the linear part of the Tauc's plot, $\alpha h\nu$ is comprised between $8 \cdot 10^6$ and $1.3 \cdot 10^7$ eV/m. Doing the extrapolation of the simplified and complete version leads to an optical bandgap of 3.308 and 3.312 eV, respectively. If the reflection is neglected, the absorption is always overestimated and the bandgap is slightly underestimated.

In a thin film on a thick substrate (here, ZnO or AZO thin film on a glass substrate), constructive or destructive interference appear depending on the thickness, the wavelength and the incidence angle. This means that the reflection will not be constant as a function of wavelength, even if the refractive index is constant. In normal incidence, the maxima of reflection correspond to the minima of transmission. However, in our setup the reflection is measured with an angle of incidence around 10° while the transmission is measured with a normal incidence, meaning that the peaks of transmission and reflection would not perfectly coincide. This means that even the equation 3.8 should be corrected to take the incidence angle into account. However, the simplified equation is a good approximation for samples that show variations of bangap greater than ~ 0.1 eV.

3.3 Multi-beam Optical Stress Sensor (MOSS)

When a stressed thin film is deposited on a thick substrate, a couple is applied on the substrate that bends as a reaction. The variation of curvature due to this phenomenon is characterized by the Stoney's formula:

$$\int_{0}^{h_{f}} \frac{\sigma(h)}{h_{f}} \mathrm{d}h = \langle \sigma_{f} \rangle = \frac{Y_{s} h_{s}^{2}}{6h_{f}} \Delta \kappa, \qquad (3.10)$$

where $Y_s = E/(1 - \nu)$ is the biaxial modulus of the substrate (182 GPa for silicon and 92 GPa for glass), h_s and h_f are the thicknesses of the substrate and the film, respectively, and h is the distance from the surface of the substrate. $\langle \sigma_f \rangle$ is the average stress in the thin film. $\Delta \kappa$ is the variation of curvature due to the applied stress.

Measuring the internal stress in a thin film is difficult but measuring the variation of curvature is possible with a profilometer, or with an optical measurement. The advantage of the optical method is that it can be done in-situ during deposition. The optical method that was used here is called Multi-beam Optical Stress Sensor (MOSS) and is described in Figure 3.4.

An array of 3×4 parallel laser beams are sent and reflected on the sample and the reflection is captured by a CCD camera. To avoid noise from the plasma discharge, a band pass filter (660 ± 4 nm) was mounted in front of the CCD camera. When the sample bends, the reflected beams are not parallel anymore and the distance between the spots in the camera changes and can be related to the variation of curvature. The position of the spots is defined as their geometric center (centroid), allowing to have a spatial resolution smaller than the size of one pixel. The variation of curvature is then used to calculate the stress in the thin film thanks to Stoney's formula. The variation of the distance between the spots with the curvature is represented in Fig. 3.5.

The incident parallel beams are separated by a distance d_0 . After reflection a distance d_0 is also measured in the CCD if the substrate is flat, and $d = d_0 + \delta d$ if the sample is curved. If the sample has a radius of curvature R, and the lasers have an incidence angle α , the distance



Figure 3.4: Multi-beam Optical Stress Sensor (MOSS). The stress in a thin film can be calculated from the variation of curvature thanks to Stoney's formula. To measure the curvature accurately, parallel laser beams are sent to the substrate and reflected to a CCD camera. When the substrate bends the distance between the spots in the CCD varies and the variation of curvature is directly proportional to the spots distance variation.

between the spots on the sample is given by:

$$D = \theta \cdot R = \frac{d_0}{\cos \alpha}$$
$$\Rightarrow \theta = \frac{1}{R} \frac{d_0}{\cos \alpha} = \kappa \frac{d_0}{\cos \alpha}$$
(3.11)

considering that θ is small. The distance between the spots in the CCD camera d is given by:

$$d = d_0 + \delta d = d_0 + 2L\sin\theta \simeq d_0 + 2L\theta \tag{3.12}$$

Combining equation 3.11 and 3.12, we can obtain the expression of the curvature as a function of the variation of the distance between the spots:

$$\kappa = \frac{d - d_0}{d_0} \frac{\cos \alpha}{2L} \tag{3.13}$$

where α is the incidence angle on the lasers and L is the optical path length between the sample and the CCD camera. In our equipment, $\cos \alpha/2L = 0.68 \text{ m}^{-1}$. The demonstration was here done for an initially flat sample so $\kappa = \Delta \kappa$. It can be shown that the variation of curvature of an initially curved sample has the same expression as long as the hypotheses of linear mechanics are respected, and θ can be considered as a small angle.

The variation of curvature $\Delta \kappa$ before and after the deposition gives the average stress but no information on the stress profile. Here $\Delta \kappa$ is measured continuously during the deposition, and is proportional to the product (average Stress)×Thickness (noted as *ST* hereafter):

$$\Delta \kappa \propto ST = \langle \sigma_f \rangle|_{e(t)} \cdot e(t) = \int_0^{e(t)} \sigma(h, t) dh$$
 (3.14)

where e(t) is the deposited thickness as a function of the time t, $\langle \sigma_f \rangle|_{e(t)}$ is the average stress in the film at a thickness e(t), and h is the distance perpendicular to the surface of the substrate. What is actually measured is the value of the curvature as a function of time, not as a function of thickness. The time scale is then converted in a thickness scale by



Figure 3.5: Variation of the distance between the reflected spots with the curvature of the sample.

measuring the final thickness and assuming a constant deposition rate, $v_{dep}{:}$

$$\frac{\partial}{\partial t} = \frac{\partial e}{\partial t} \frac{\partial}{\partial e} = v_{dep} \frac{\partial}{\partial e}$$
(3.15)

Thanks to the Leibniz formula, the time derivative of ST can be evaluated as:

$$\frac{\partial}{\partial t} \left(\langle \sigma_f \rangle \cdot e \right) = \int_0^e \frac{\partial \sigma(h, t)}{\partial t} dh + \sigma\left(e, t\right) \cdot \frac{\partial e}{\partial t}$$
(3.16)

For more convenience ST is often plotted as a function of e. The slope of such graph is then:

$$\frac{\partial}{\partial e}(\langle \sigma_f \rangle \cdot e) = \int_0^e \frac{\partial \sigma(h,t)}{\partial t} \cdot \frac{1}{v_{dep}} dh + \sigma(e,t)$$
(3.17)

In this work, no stress relaxation was observed in ZnO nor AZO thin films, meaning that every time dependence of the stress can be neglected. In this case, the slope of ST equals the stress profile in the film:

$$\frac{\partial}{\partial e} \left(\langle \sigma_f \rangle \cdot e \right) = \sigma(e) \tag{3.18}$$

3.4 Sputtering

The sputtering of ZnO and AZO will be detailed in Chapter 4 and 5, and only the general principles are depicted here.

Sputtering principle

In sputtering, a target of the base material for the wanted sample is kept in a vacuum chamber. A sputtering gas (typically argon) is then introduced in the chamber and a plasma is ignited by applying a negative voltage on the target, while the chamber is grounded. Ar^+ ions are therefore accelerated toward the target and impact it, extracting some atoms. The sputtered atoms then redeposit in the chamber, including on the sample placed in front of the target. During this thesis, the distance between the sample and the target was kept at 122 mm. The applied voltage can be RF or DC. Typically, DC voltage is used for conductive targets and RF is used for insulating targets. Indeed, if a DC voltage is applied to an insulating target, the Ar^+ ions will positively charge it and the target will finally repel the Ar^+ so no more sputtering will occur. To avoid this, an RF voltage is applied so the target is hit successively by Ar^+ and electrons, remaining uncharged on average.

When an argon ion hits the target, it gives energy to the atoms of the target and if this energy is larger than the bonding energy, the atom is sputtered. The sputtering yield is therefore dependent on the target material.

When argon is used as sputtering gas, the deposited material has almost the same composition as the target since the sputtering is a mechanical ablation. In thermal evaporation for example, the deposition of an alloy is not straightforward since the source material is melted and the deposition rate depends on the vapor pressure of each component of the alloy. As said previously, the sputtering yield depends on the target material so one could expect a similar phenomenon in sputtering. However in sputtering the target remains solid, meaning that if an element is sputtered faster the surface of the target will be enriched with the other element, compensating the lower sputtering rate. One situation where the stoichiometry is not exactly the same is when the target is a compound material such as an oxide or a nitride. In this case, the deposited material can be partially reduced due to some O/N atoms that are sputtered and evacuated through the pump.

To avoid the reduction of the target material, or even deposit an oxide (nitride) with a metallic target, it is possible to add a reactive gas such as oxygen (nitrogen). This is called reactive sputtering and it was used in this thesis to deposit ZnO (Al doped ZnO), with a Zn (Zn_{98.68}Al_{1.32}) target. Even for reactive sputtering, argon is used because it has a higher sputtering yield than oxygen or nitrogen. In addition, using a pure reactive gas would lead to the poisoning of the target which is undesirable in some applications (see Chapter 4 and 5 for more details).

To ignite the plasma, a sufficient density of charged elements must be present (sufficient pressure and ionization rate). However, it is sometimes interesting to decrease the pressure to obtain a denser film or to change the stress in the deposited film (see Chapter 4 and 5). Moreover, charged elements hitting the sample can be damageable for the properties. To limit these problems, the plasma can be confined near the surface of the target with a magnetic field. Permanent magnets where here placed under the target as depicted in Fig. 3.6. This magnetic confinement is responsible for the circular shape of the racetrack, leading to a target surface varying with the erosion as it will be discussed later. The target is electrically connected through Oxygen-free High Conductivity (OFHC) copper to apply the voltage, and allow a good evacuation of the heat. Water circulates in this copper under the target to maintain a constant temperature during deposition. If the applied power is high and the thermal conductivity of the target is low, a thermal gradient can occur anyway. In ceramic targets, such temperature gradients can cause cracks if the variation of applied power is too fast and a ramp must be used when the voltage/power is changed. In this thesis, metallic target were used so the variation of voltage was applied without any ramp. The magnets configuration depicted in Fig. 3.6 is used for sputtering of non magnetic elements since the closed magnetic field lines create a strong confinement, hence a higher sputtering rate. For sputtering of magnetic elements such as nickel, this configuration leads to a high sputtering



Figure 3.6: Configuration of the sputtering guns in the sputtering machine used. Permanent magnets are used to confine the plasma near the target and water channels are used to cool the target. OFHC copper is used as electrode to apply the voltage to the target.

rate but the sputtered atoms are also confined near the target, leading to a low deposition rate. In this situation, the central magnet is flipped to have the same orientation as the exterior magnets, leading to open magnetic fields lines that allow the magnetic elements to escape.

3.4.1 Sputtering mechanisms

There are two main sputtering mechanisms. [106] When heavy ions collide a surface they transfer their energy to it and a chain reaction occurs, ejecting atoms from the surface of the target (mechanism 1). When a lighter atom such as hydrogen is used, it cannot create this chain reaction and a second mechanism takes place. The energy transferred to an atom pushes it into the surface, then it bounces back toward the outside. If the transferred energy is sufficient to overcome the potential barrier, it will be sputtered (mechanism 2). The lighter the sputtering atom, the more the mechanism 2 is favored. When argon is used as sputtering gas both mechanisms are important. Depending on the incidence angle the sputtering rate changes significantly. When the incidence angle is slightly tilted from the normal of the surface, the sputtering rate increases because the chain reactions are closer to the surface, allowing atoms to escape the target. If the incidence angle is too far from the normal, the sputtering yield decreases because neighbor atoms prevent the sputtering atoms to penetrate the target surface. For a grazing incidence, the sputtering ions are mostly reflected by the surface and transfer almost no energy to the surface. The optimum incidence angle from the surface is typically between 60 and 80° . [106]

In addition to atoms, electrons are also emitted from the target during sputtering. This has been reviewed in several books such as references [107–110]. The basic principle is that the impacting ions can transfer energy to electrons of the target and if this energy is sufficient (work function for metals, band gap plus electron affinity for nonmetals), the electron might escape the target. These ion-induced electrons are important in sputtering because their collisions with the sputtering gas ionize it, stabilizing the plasma.

3.4.2 Reactive sputtering

Non-reactive sputtering is relatively simple because the target is physically ablated by the argon plasma and the sputtered atoms are deposited on the sample, without chemical reaction. Reactive sputtering is much more complicated because the thermodynamics and kinetics of the chemical reaction have a significant effect on the sputtering process. Reactive sputtering of AlN with an Al target in an $Ar+N_2$ plasma is a well-studied situation that will be used as example in this section. A typical evolution of the deposition rate and pressure is shown in Fig. 3.7 It is well-known that the sputtering yield of AlN is significantly lower than the one of pure Al, leading to this hysteresis behavior. The evolution of the sputter erosion rate and pressure with the reactive flow can be explained as follows:

• A The plasma only contains Ar so that pure aluminum is deposited

- AB The reactive gas introduced reacts with the sputtered particles in the plasma, on the sample and on the chamber walls. There is not enough reactive gas to completely nitride the deposited aluminum and an under-stoichiometric AlN_x is deposited, with x < 1. The target is sputtered faster than it is nitrided, leading to a metallic target with a slow decrease of the sputter rate. Since the additional gas reacts completely with the sputtered aluminum, no significant increase of the pressure is observed. This is called the metallic mode.
- BC There is enough reactive gas to completely nitride the deposited aluminum (stoichiometric AlN) and the target also begins to be significantly nitrided so the sputtering rate decreases (lower sputtering yield for AlN). A decrease of the sputtering rate leads to a decreased amount of sputtered aluminum that can react with nitrogen so there is now an excess of nitrogen in the chamber. This additional nitrogen reacts with the target, leading to a decreased sputtering rate, a lower nitrogen consumption, etc. The difference of sputtering yield between Al and AlN is therefore the origin of the very steep decrease (increase) of the sputtering rate (pressure). B and C both lead to stoichiometric AlN, but B has a much higher deposition rate so it is preferred.
- CD The target is completely nitrided and it corresponds to the "poisoned" regime. If oxygen is the reactive gas (for ZnO or AZO deposition for example), the regime can also be called "oxidized regime". In this regime, the sputtering rate is almost stable since the state of the target does not change significantly. The additional nitrogen does not react so it stays in the chamber and the pressure increases.
- **DE** As the nitrogen is decreased, the pressure decreases linearly and the sputtering rate is almost constant.
- **EF** The target begins to be sputtered faster than it is nitrided, so there is more aluminum deposited that reacts with nitrogen, so there is less nitrogen to nitride the target, etc. leading to an



Figure 3.7: Typical hysteresis behavior of the sputter erosion rate and pressure during reactive sputtering as a function of the reactive gas flow, for example an Al target in a argon + nitrogen (reactive gas) plasma to deposit AlN.

inverse phenomenon as in **BC**. The transition does not occur at the same partial pressure between **BC** and **EF** because of the different initial sputtering yield of the target.

• **FA** Metallic regime similar to **AB**: all the nitrogen is consumed to react with the deposited aluminum.

Different parameters can influence the importance of the hysteresis since it comes from an equilibrium between the poisoning and erosion of the target. A first parameter that will increase the importance of the hysteresis is the ratio between the sputtering yield of the metal and the compound target. Another important parameter is the ratio between the area of the target and the chamber. A small target and a high pumping speed tend to decrease the hysteresis. For more information, see Ref. [111–113].

In the experiments performed during this thesis on ZnO and Al:ZnO, no significant hysteresis could be observed. To avoid reproducibility problems due to a possible slight hysteresis, the target was always cleaned with a pure Ar plasma, with a closed shutter, before deposition to reach a metallic surface. The oxygen is then introduced in the same concentration as during the deposition and the plasma is maintained around 5 min to reach a steady state. Only then the shutter is opened and the deposition started.

3.4.3 Description of the system

The sputtering experiments during this thesis were performed in a chamber from AJA, equipped with a turbo-molecular pump with a maximum pumping speed of 315 l/s, calculated as the ratio between the gas flow and the pressure. The effective pumping speed can be decreased thanks to an automatic pressure control valve between the chamber and the pump. The base pressure in the chamber is around 10^{-7} mbar before deposition, measured with a hot-filament ionization gauge. The gas flow of O_2 and Ar are regulated by independent mass flow controllers. The pressure in the chamber during deposition is measured with a capacitance vacuum gauge and kept constant at 2.7×10^{-3} mbar. This type of gauge is used because it measures the pressure independently of the type of gas, which is interesting for reactive sputtering where different gases are used simultaneously, in variable proportions. To insure a good uniformity, the samples were rotated at 45 rpm and disposed at a relatively large sputtering distance (122 mm). This large distance also minimizes the problem of negative oxygen ions bombardment. To limit the creation of oxygen ions furthermore, the oxygen is introduced in the chamber through small holes at the level of the substrate, far from the target where the plasma is the densest. The argon is introduced at the bottom of the chamber. A schematic of the chamber is presented in Fig. 3.8, and pictures are visible in Fig. 3.9.



Figure 3.8: Schematic of the sputtering chamber used during this thesis.



Figure 3.9: *Pictures of the top (sample holder) and bottom (targets) of the inside of the sputtering system.*

During deposition the chamber walls, the chimney around the targets and the shutters are grounded, the potential is applied to the target, and the sample is kept floating.

3.4.4 Temperature control

As it will be discussed in Chapters 4 and 5, the deposition temperature is a very important parameter in sputtering. However, it was not deeply studied in this thesis because it is not possible to heat a sample patterned with photoresist without damaging the lithography process. Post-deposition annealing was therefore preferred. Another reason is that the control of temperature in a vacuum system can be tricky due to the very low thermal conductance. This means that a thermometer that is not placed in direct contact with the sample can give a measurement significantly different from the real temperature of the sample. Unfortunately in our system the temperature cannot be measured directly on the sample during deposition. The difficulty comes from the fact that the sample holder is rotated during deposition to insure a good uniformity. Two thermometers are available in our chamber. One that is between the sample and the heating lamps. Because it is closer to the lamps and with a better thermal anchoring than the sample, we can assume that it measures a temperature higher than the real temperature of the sample. This thermometer is the one used to regulate the temperature. The second thermometer is on a mobile arm that can be placed in contact with the sample. However, it would be between the sample and the sputtering target, inducing important shadowing effects during deposition. Moreover, the contact with the rotating sample could induce scratches. This thermometer can therefore not be used during deposition. It was used only once on a test sample to make a comparison with the thermometer used for regulation. The result is shown in Fig. 3.10. Since the thermometer on the sample was not in perfect thermal contact with the sample, it probably underestimates a little the temperature. However, this experiment shows that there is a poor control of the temperature in this equipment. Therefore, the few experiments where the deposition temperature is varied should be seen as qualitative



Figure 3.10: Temperature measured directly on the sample versus temperature measured by the thermometer used for the regulation.

more than quantitative regarding the deposition temperature.

3.5 Piezoresisance measurement: substrate bending

One common method to strain thin films is to deposit them on a substrate and then bend the substrate. When the substrate is bent, a linear strain profile appears perpendicularly to the substrate, going from tension to compression. If a thin film is deposited at the surface of the substrate, the strain in the thin film can be considered as constant. In this thesis we used this technique to measure the importance of the piezoresistive effect in ZnO and AZO thin films deposited on silicon substrates. The silicon substrates were oxidized over a thickness of 300 nm to ensure a good insulation between the studied thin films and the substrate. Note that the use of silicon substrates limits the applied strain to ~0.1% before fracture of the substrate. This type of substrate was however preferred over polymer substrates to allow high temperature annealings. A picture of the 4-points bending system, a schematic of the system and the conventions used to calculate the applied stress are



Figure 3.11: Picture and schematic of the bending system used to bend the substrates, to apply a strain on a thin film at the surface of the substrate. The applied strain can be in tension or compression depending on the orientation of the bending.

presented in Fig. 3.11. The substrate is placed between the cylinders and the bottom part of the system is pushed up of a measured distance Δf . When the bottom part goes up, the cylinders apply an unknown force F that bends the substrate.

The first hypothesis we make to calculate the strain at the surface of the substrate is that the substrate is a rectangular beam. This hypothesis can be justified because between the cylinders that apply the force, the width of the substrate varies slowly, and outside of the cylinder the beams are free so they will not influence the deflection of the substrate. We also neglect gravity and consider that only the force F is responsible for the bending of the substrate. Finally, we consider that the thin film does not influence the mechanical behavior of the substrate since it is

more than 1000 times thinner.

The symmetry of the problem allows to study only half of it, for x > 0, with x = 0 corresponds to the center of the substrate. Because of the symmetry of the system, we can also easily deduce that the forces applied in each cylinder are equal to each other. With beam theory, we can calculate the shear stress (T) in the substrate, as well as the bending momentum (M) and the deflection (f). The local curvature radius of the substrate is noted R, the distance to the neutral axis is z, the thickness of the substrate is t, the length of the substrate is 2L, and we consider that the neutral axis is in the middle of the substrate. The shear stress and bending momentum profiles are presented in Fig. 3.12.

Since there is no average stress on the neutral axis, the length of the neutral axis in an infinitesimal section of the substrate is constant and noted l. The surface of the substrate however has a varying length due to the bending. The face with tensile stress will have a final length $l+\delta l$, as noted in Fig. 3.12. If we assume that the stress profile is linear along the z-axis, and if we define the strain as $\delta l/l$ (small strain hypothesis), we obtain:

$$\frac{l}{R} = \frac{l + \Delta l}{R + z}$$

$$\varepsilon = \frac{\Delta l}{l} = \frac{z}{R}$$
(3.19)

With the Hooke's law $\sigma = \varepsilon E$, with E the Young's modulus, we obtain:

$$\sigma = \frac{zE}{R} \tag{3.20}$$

We can link the bending momentum and the curvature radius:

$$M = \int_{-t/2}^{t/2} \sigma z . dz = \int_{-t/2}^{t/2} \frac{E z^2}{R} dz$$
$$M = \frac{E t^3}{12R}$$
(3.21)

Simple geometric considerations can relate the second derivative of the deflection and the curvature radius:



Figure 3.12: Shear stress and bending momentum profile in the substrate, and definition of the dimensions of an infinitesimal section of the substrate.

$$\frac{1}{R} = -\frac{d^2 f(x)}{dx^2}$$
(3.22)

Combining equations 3.21 and 3.22 we can obtain the following equation:

$$\frac{d^2 f(x)}{dx^2} = -\frac{12}{Et^3} M(x) \tag{3.23}$$

What we want to know is $\varepsilon(z = t/2, x = 0)$ because it corresponds to the strain applied to the Hall bar where the electrical measurement is performed. The Hall bar is not strictly located at x = 0, but since the bending momentum is constant in the interval [-a, a], the strain at the surface of the substrate is constant in this interval. Combining equations 3.19, 3.21 and the bending momentum given in Fig. 3.12, we obtain at z = t/2 and x = 0:

$$\varepsilon = F \frac{6(d-a)}{Et^2} \tag{3.24}$$

Unfortunately, the force is unknown, only the difference of deflection between a and $d f(a) - f(d) = \Delta f$ is measured. Therefore, we must calculate this difference of deflection as a function of the applied force. By integrating twice the bending momentum it is possible to determine the deflection f(x) for the different parts of the substrate ([0, a], [a, d], [d, L]). Several constants must be determined after the integration and the following conditions are used to determine them: we define f(0) = 0 and due to the symmetry of the problem f'(0) = 0. There must also be continuity of f(x) in a and d. Finally, the deflection between a and d is given by:

$$f(x) = -\frac{6F}{Et^3} \left[-\frac{x^3}{3} + dx^2 - a^2x + \frac{a^3}{3} \right]$$
(3.25)

Therefore, the difference of deflection Δf is given by:

$$\Delta f = \frac{12F}{Et^3} \left[\frac{d^3}{3} + \frac{2}{3}a^3 - a^2d \right]$$
(3.26)

Finally, combining equations 3.24 and 3.26, we obtain the relation between the difference of deflection Δf (measured) and the strain in the thin film ε :

$$\varepsilon = \frac{3}{2} \frac{t(d-a)}{d^3 + 2a^3 - 3a^2 d} \Delta f$$
(3.27)

3.6 Hall measurements

The Hall effect is the occurrence of a transverse voltage in a conductor when a magnetic field is applied perpendicularly to the current. The classic geometry to observe this phenomenon is the Hall bar, depicted in Fig. 3.13.

3.6.1 Hall bar

The Hall bar consists of a bar of the studied material with lateral contacts. The current flows in the x-axis inducing a longitudinal voltage V_x . A magnetic field B_z is applied perpendicularly to the plane of the Hall bar. The charge carriers (electrons or holes) responsible of the current have an average velocity drift v_x , perpendicular to the magnetic field and therefore experience a force along the y-axis:

$$F_y = q(v_x \cdot B_z) \tag{3.28}$$

where the velocity drift is defined by:

$$I_x = nq \cdot v_x \cdot wt \tag{3.29}$$

with n the charge carrier density, q the charge of the charge carriers, w and t the width and thickness respectively. This force will induce an accumulation of charge in one side of the Hall bar, creating an electric field along the y-axis, $E_y = -V_H/w$. In steady state, the forces due to the electric and magnetic fields must cancel each other, leading to:

$$V_H = \frac{I_x B_z}{nqt} \tag{3.30}$$

The Hall voltage thus gives the charge carrier density and the type of charge carrier (holes or electrons) depending on its sign. The resistivity is given by the longitudinal voltage, assuming that it is isotropic:

$$\rho = \frac{V_x}{I_x} \frac{wt}{L} \tag{3.31}$$

With the resistivity and the charge carrier density, it is possible to have the charge carrier mobility, μ , thanks to the Drude's model:

$$\rho = n e \mu \tag{3.32}$$

3.6.2 Van der Pauw geometry

Hall bars require a patterning of the studied layer, which is not always possible, and requires more process. The Van der Pauw method can be used on square samples, much easier to produce. The equipment used in this thesis to perform the Hall measurements was a HMS-3000 from Microworld in the Van der Pauw geometry. The probes in this equipment are gold-plated to have a good electrical contact. If the contact is not good enough with the probes, some metallic pads can be deposited at the corners of the square. With the AZO samples the contacts between the probes and the sample were ohmic so no metallic pads were deposited.

The sample is here a square with contacts at each corners numbered from 1 to 4 in a counter-clockwise order. The current between contacts



Figure 3.13: Hall bar geometry to perform Hall measurements.

i and *j* is noted I_{ij} , and the voltage is noted $V_{ij} = V_j - V_i$. The sheet resistance R_s of a material is defined as:

$$R_s = \frac{\rho}{t} \quad [\Omega/\Box] \tag{3.33}$$

Since the Van der Pauw geometry uses four contacts, no current flows in the probed used to measure the voltage, and the contact resistance is not included in the measured resistance. The current is applied between two contacts of a same side of the square (1 and 2 for example) and the voltage is measured on the opposite side of the sample (between 3 and 4). The resistance is then measured for every rotation of this configuration and the average value R is taken. This average resistance is linked to the sheet resistance by the following relation:

$$R_s = \frac{\pi R}{\ln 2} \tag{3.34}$$

To measure the charge carrier density and mobility, a magnetic field is applied perpendicularly to the sample. In this case, a permanent magnet of 0.55 T was used. The current is then imposed between opposed corners of the sample (1 and 3 for example) and a transverse voltage appears due to the magnetic field (between 2 and 4). The transverse voltage (Hall voltage) is related to the carrier density by:

$$V_{24} = V_H = \frac{IB}{nqt} \tag{3.35}$$

Note that this relation is only valid in theory, where the sample is perfectly symmetrical so that $V_{24} = 0$ when B = 0. In practice, the transverse voltage due to the asymmetry of the sample can be much larger than the Hall voltage due to the magnetic field. The measurement is therefore done with a positive and negative magnetic field and the Hall voltage is given by:

$$V_H = \frac{V_{24,B} - V_{24,-B}}{2} \tag{3.36}$$

Depending on the sample, the transverse voltage was between the same order of magnitude and two orders of magnitude larger than the Hall voltage. This means that the calculation of the charge carrier density can be the result of the measurement of a small variation of a large quantity, leading to low accuracy in some samples.

3.7 XeF₂ etching

 XeF_2 is a gas used to etch silicon, with an excellent selectivity to other common MEMS and semi-conductor materials. XeF_2 gas is obtained by sublimation of XeF_2 crystals. The vapor pressure as a function of temperature is shown in Fig. 3.14. XeF_2 etches silicon according to the following reaction:

$$2XeF_2 + Si \to 2Xe_{(g)} + SiF_{4(g)} \tag{3.37}$$

It is important to have a clean, oxide-free and dry surface to obtain a uniform etching. A HF dip followed by a rinse and dehydration can achieve the required clean surface but is not compatible with all materials. An argon plasma has also been proven to work to obtain a clean



Figure 3.14: Vapor pressure of XeF_2 as a function of temperature. Taken from Ref. [114].

surface. If water is adsorbed on the surface of silicon, a thin silicon fluoride polymer layer may form, reducing the etching rate and uniformity. The equipment used during this thesis is a Xetch e1 from Xactix.

The etching can be done with continuous exposure to XeF₂ or with pulses. The latter one was used in this work. The XeF₂ crystals are heated around 30°C and are sublimated in an expansion chamber. When we refer to the XeF₂ pressure, it corresponds to the target pressure in the expansion chamber. When the target pressure is reached, the expansion chamber is opened to the etching chamber where the sample is placed. After a certain time (pulse time), the valve between the expansion and etching chambers is closed and they are both pumped down to vacuum. The vacuum is here only a primary vacuum (around 2×10^{-2} mbar) obtained with a scroll pump. This cycle is referred to as a "pulse" and is repeated until the sample is completely released. An optical microscope has been mounted on top of the Plexiglas chamber, allowing to observe the release in real-time. This is especially useful for XeF₂ because the etching rate depends strongly on the amount of exposed silicon, hence on the sample.

Three big advantages of XeF₂ release are: they do not require the depos-

ition of a sacrificial layer, they have an almost infinite selectivity with lots of materials and the gaseous release avoids stiction. The latter two advantages must however be discussed.

Stiction with XeF₂

A common way to release a MEMS is to etch the substrate or a sacrificial layer with wet etching. The MEMS is then free-standing but in a liquid environment. If it is dried without care, the liquid will dry last between the MEMS and the substrate. This remaining liquid induces capillarity forces that stick the MEMS to the substrate, making it unusable. This phenomenon is called stiction. To prevent this, a critical point dryer (CPD) is required. After the end of the release, the sample must be rinsed in several baths of isopropanol (IPA) before being introduced in the CPD. The IPA is then replaced by liquid CO_2 , the pressure and temperature are increased to obtain supercritical CO_2 . The pressure is then decreased down to atmospheric pressure and the sample is cooled down to evaporate the CO_2 . The goal of this process is to avoid interfaces between liquid and gaseous phases so that no capillarity forces are present, and stiction can be avoided. Another way to avoid stiction is to use dry release methods with gases or plasma.

An example of released lab-on-chip samples is presented in Figure 3.15. The comparison is done between samples with and without stiction. The samples with stiction go out of plane, meaning that the strain measurement is erroneous because the out-of-plane displacement can not be measured.

Stiction during XeF_2 release has, to the best of our knowledge, never been reported before. The first test performed after the installation of the equipment revealed no stiction. After some months however stiction began to be observed. The origin of this phenomenon is not understood yet but seems to come from some kind of contamination.

Contamination of the sample however does not seem to be the cause of the stiction since samples cleaned with an argon plasma and/or an HF dip is not enough to avoid stiction even though the resulting surface



Figure 3.15: Lab-on-chip samples released that exhibit no stiction (Top) and stiction (Bottom).
should be perfectly clean silicon. This could indicate a contamination of the XeF_2 equipment with an unknown contaminant.

Electrostatic forces can also be excluded since stiction has also been observed between metallic beams short-circuited to the substrate. Capillarity forces can be excluded since no liquid is present in the chamber. Some authors have proposed the van der Waals forces or the Casimir effect as a possible source of stiction in MEMS [115, 116], however it would not explain why it was not observed during the first releases. Up to now, the origin of the observed stiction is still unknown.

Selectivity Si₃N₄:Si in XeF₂

An almost infinite selectivity has been observed with lots of materials (Pt, Pd, Al, Ni, Cr, ZrNi, ZnO, AZO, Al_2O_3 , ZrO_2) but silicon nitride is an exception and is slightly etched. Actually, XeF_2 does not etch silicon nitride, but silicon etching byproducts do. These byproducts are however unavoidable if the silicon substrate is used as a sacrificial layer. Several tests were done to increase the selectivity. An exact comprehension of the best way to increase the selectivity still has to be achieved, and only general observations are discussed here.

- The first observation is that the pulses must be short, so that the byproducts are quickly evacuated and do not etch Si_3N_4 too much. Instead of simply pumping the gas away, injecting another gas such as nitrogen in the chamber can be done to stop the etching more quickly. This seems to be the best way to increase the selectivity.
- Decreasing the amount of etched silicon reduces the formation of byproducts and decreases the silicon nitride etching. This can be done by modifying the design of the MEMS to have as little etched silicon as possible. However, the released beams must be placed on etched silicon so local production of byproducts is unavoidable. Using SOI substrates with a thin top silicon might be a solution to reduce the amount of etched silicon, but favors the stiction.

- Diluting XeF₂ in another gas can slightly improve the selectivity, even though it was not clearly observed in our case. Oxygen, water and nitrogen were tested. The best results should be obtained with hydrogen according to Ref. [117], which was not tested here. The role of the second gas would be to cool down the sample that heats due to the etching of silicon.
- The surface state of the silicon nitride seems to have a major impact on its etching rate. When stiction was observed, the silicon nitride was almost never etched, which seems to confirm that a surface contamination is the cause of the stiction, and that this contamination also protects the silicon nitride.
- A slight oxidation of silicon nitride strongly decreases its etching rate. Indeed, it was observed that an oxygen plasma before the release tends to protect the Si₃N₄ for the first pulses. After some pulses, the etching rate seems to go back to the value observed for non-oxidized Si₃N₄. If the oxygen plasma is short enough, the oxidized silicon surface is thin enough to be etched by XeF₂. If the oxygen plasma is too long, the oxide layer formed on the silicon cannot be etched. In this situation, an HF dip or a long argon plasma must be done to remove the SiO₂ layer. In both cases the protection of the Si₃N₄ disappears.

In the first tests performed during this thesis an almost infinite selectivity for silicon nitride was observed on some samples when the XeF₂ pulses were short enough (2 s). Later, this selectivity dropped to around 1:200, meaning that the actuators are almost completely etched at the end of the release. The etching parameters change significantly the selectivity but even with the same etching parameters and sample preparation, the selectivity changes a lot from a sample to another meaning that the deposition of the silicon nitride layer has varying properties from one time to another one. After the production of the first samples, a leak in the water cooling system of the LPCVD furnace has been detected and fixed. One hypothesis is that for the samples with an infinite selectivity, some water was present during the Si₃N₄ deposition, creating an oxynitride (much closer to Si₃N₄ than SiO₂ though). This would be coherent with the protection of the nitride observed after an oxygen plasma.

Several annealings have been done at temperatures between 700 and 1000°C, under nitrogen and water vapor, between 15 min and 2 hours. Note that the furnace under nitrogen also contains residual oxygen. The etching rate of these samples dropped significantly but was still not as good as the first tests. A reason could be that the annealing densifies slightly the nitride, increasing a bit its chemical stability, but the modification is mainly in the surface because the oxygen/water cannot diffuse deeply in the silicon nitride. Only a tiny passivation is therefore created on the surface. The problem is that only the top surface is protected with this technique, not the bottom surface. During the release the byproducts are created and confined under the unprotected bottom surface, etching the actuators. Introducing some water or oxygen during the silicon nitride deposition to obtain a bulk $Si_3N_{4-\varepsilon}O_{\varepsilon}$ with a small ε seems to be the best way to obtain an actuator that has an almost infinite selectivity in XeF_2 . The advantage of a bulk oxidation of the actuator instead of a surface passivation is also that it can be cleaned with HF or an argon plasma and still be protected. The actuator must however have a stoichiometry close to Si₃N₄ because SiO₂ exhibits compressive stress, hence cannot be used as an actuator.

The deposition of such a layer of (oxy)nitride must still be optimized but seems to be a very promising way to obtain a nearly infinite selectivity, combined with the use of short XEF₂ pulses followed by pulses of an other inert gas to purge the chamber from the byproducts.

Chapter **4**

Sputtering of ZnO

It was stated in Chapter 1 that intrinsic ZnO is not a suitable material for transparent electrodes and this will be demonstrated in this chapter, and confirmed in chapter 5 where a comparison will be done with doped ZnO. However, ZnO is here studied as a base material to understand how the growth conditions influence the defects and properties in ZnO, and in AZO after that. It will also be demonstrated that ZnO can also be of interest for transparent strain gauges deposited at room temperature. Indeed, transparent and flexible electronics is more and more studied and this field of application implies polymer substrates and large deformations.

To quantify the deformation, piezoresistors are often used and can be grouped mainly in two families, metals and semi-conductors. Piezoresistors can be characterized by their gauge factor (GF)

$$GF = \frac{\Delta R/R}{\varepsilon} = \frac{\Delta \rho/\rho}{\varepsilon} + 1 + 2\nu, \qquad (4.1)$$

with R the resistance, ρ the resistivity, ε the strain and ν the Poisson coefficient.

Metallic piezoresistors are easy to process and can be deposited at low temperature. However, they are not transparent and have a small gauge factor because the variation of resistance is mainly due to the geometric term $1 + 2\nu$, leading to gauge factors for metallic thin films comprised between 2 and 3. [118–120] In addition, the piezoresistors need to be large to have a significant resistance due to the low resistivity of metals.

Semi-conductors can have a much larger gauge factor because the strain changes the band structure, hence the charge carriers mobility and density. Typical semiconductors for piezoresistors are Si (GF between 16 and 45 for polycrystalline silicon [121] and up to 200 for single crystal [122]), SiC (GF around 30 [123]) or diamond (GF between 2000 and 3836 for single crystal and between 10 and 100 for polycrystalline [124]). Silicon thin films can be deposited at relatively low temperature on polymer substrates [125] but are not transparent and their small bandgap makes them very sensitive to light and temperature. Diamond is transparent and has a low dependence to temperature but needs to be deposited at high temperature. SiC has more than 200 polytypes [126] and needs to be deposited at high temperature too.

Here, we propose ZnO as a candidate for piezoresistors in transparent electronics because it is a transparent material with a large bandgap (3.3 eV) and has a gauge factor greater than metals. Its possible high resistivity allows to miniaturize the piezoresistors dimensions and achieve low power consumption. Contrary to other usual semiconductors, it can be deposited by sputtering at room temperature on almost any kind of substrate (crystalline, amorphous, polymer) and naturally has a wurtzite structure with a (0002) preferential orientation.

Different parameters can be changed to tune the electro-optical properties of ZnO during reactive sputtering such as substrate temperature or oxygen partial pressure. Deposition temperature has already been discussed in a previous publication [87] so it will not be discussed here, even though it has a significant influence. All the depositions have been done at room temperature. The parameter that is particularly studied here is the oxygen partial pressure. This parameter is of utter importance for electronic properties - hence optical properties too - because it changes the stoichiometry. It is well known that stoichiometric ZnO is an insulating material, transparent to visible light with a bandgap of 3.3 eV. With reactive sputtering it is possible to change these properties by changing the stoichiometry, i.e. having ZnO_x with x smaller than 1. This creates an intrinsic doping that changes the charge carrier mobility and density, and defects that alter the optical properties. Typically, the defects are oxygen vacancies and/or zinc interstitials when the sputtering is done in zinc-rich conditions, and zinc vacancies and/or oxygen interstitials in oxygen-rich conditions. [26, 127–129]

During deposition, it also changes growth mechanisms hence the internal stress on a wide range. These internal stresses are important because they are added to the stress applied when the substrate is bent. To avoid a premature cracking of the layer it is thus important not to have too high internal stress.

When oxygen partial pressure is varied in reactive sputtering, it goes from a metallic mode (low oxygen concentration, the surface of the target is metallic) to an oxidized mode (high oxygen concentration, the surface of the target is oxidized), through a transition mode. The transition mode is often avoided in the industry because of its instability and difficulty to have reproducible results. However, this transition mode is scientifically interesting because it allows to largely tune the properties of a material and study the effect of each parameter.

It was observed in the literature that the piezoresistance of ZnO thin films obtained by non-reactive sputtering exhibited positive gauge factors in the range 1-3 [126], however, their measurements were done with two-contact method and it was shown with ZnO nanowires that in this configuration the piezotronic effect can be dominant over piezoresistance. [130, 131] For these nanowires, the gauge factor varied a lot from one sample to another, but the average gauge factor was around -16. Piezoresistivity of quasi-one-dimensional ZnO nanowires has recently been performed in uniaxial tension thanks to the push-to-pull method and a gauge factor of -3.3 [132] or -24 [133] was measured.

In this chapter (published as Ref. [5]) we study the effect of the oxygen partial pressure on the gauge factor and electro-optical properties of ZnO thin films deposited at room temperature. We also analyze the growth mechanisms thanks to an in-situ measurement of the internal stress.

4.1 Experimental method

ZnO thin films were deposited by DC magnetron reactive sputtering from a Zn target (99.99 % purity) in a mixture of argon and oxygen, with a current fixed at 100 mA. The sputtering chamber is described in section 3.4 Two types of substrates are used: 2.5×2.5 cm² squares of 400 μ m-thick extra clear float glass with low iron content, and 380 μ m-thick oxidized silicon substrates of 3 inches of diameter. The oxidation was done by wet oxidation at 1000°C to obtain a 300 nm-thick layer of SiO₂. The glass wafers are used for optical measurements. The oxidized silicon wafer are used for (piezo)resistivity measurements and in-situ monitoring of the internal stress during deposition, with the MOSS technique described in section 3.3.

Since the initial curvature of the substrate often varies as a function of the orientation, the curvature is always measured at the same position, at every rotation of the sample. The time resolution of this technique is thus of 1.3 s (45 points per minute). The variation of curvature ($\Delta \kappa$) of the sample is given by:

$$\Delta\kappa(t) = \frac{D(t) - D_0}{D_0} \cdot G, \qquad (4.2)$$

where D(t) is the average distance between the centroids, D_0 is the initial average distance between the centroids, and G is an optical parameter depending on the chamber (0.68 m^{-1} in our case). Because the lasers form a 2D mesh, the stress is measured in both in-plane directions, with no visible difference, confirming that the deposition has a central symmetry.

From eq. 3.10, when $\langle \sigma_f \rangle \cdot h_f$ is plotted as a function of the film thickness, its derivative is σ_{incr} , the instantaneous incremental stress in the film corresponding to the stress in the growing film and the relaxation of the stress in the whole film. Positive values of $\langle \sigma_f \rangle \cdot h_f$ correspond to an average tensile stress. The instantaneous error on the product stress×thickness is 1.4 GPa.nm, evaluated as twice the variance of the noise in the measurement system (σ_{MOSS}). To decrease the error on the average stress even more, the initial and final curvatures are measured for at least 5 min and the average is taken on all the *n* measurements. The error on the average stress for a 150 nm-thick film is then $2\sigma_{\text{MOSS}}/h_f\sqrt{n} = 0.62$ MPa. Curvature is measured as a function of time and needs to be converted as a function of film thickness to extract the incremental stress. The conversion of the time scale into a thickness scale is done assuming that the deposition rate is constant, as confirmed by a quartz-microbalance.

The total thickness of the films on oxidized silicon substrates is measured after the deposition by ellipsometry (SENTECH SE 850) and by crosssectional view in a FEG-SEM (Zeiss Ultra 55 field-emission gun). Ellipsometry measurements confirm the homogeneity of the samples with a variation of thickness of maximum 3% between the center and the edge of the 3 inches substrates. In the smaller parts of the substrates that are analyzed in this article (1x1 inch), the variation is on the order of 1%. The thickness of the samples on different substrates are shown in Table 4.1.

Specular transmission (T) and reflection (R) of the samples deposited on glass were measured with a spectrophotometer Specord 200 PLUS from Analytic Jena, for wavelengths between 300 and 1,100 nm with a 1 nm resolution. Transfer matrix method (TMM [134]) was used to fit the experimental curves (R and T) to obtain the thickness (h_f) , the real refractive index (n), and the extinction coefficient (k) of each material. TMM is a well-know technique in thin-film optics and is widely used in fields like photovoltaic [135] or photonics [136] to investigate simple optical systems.

After deposition, X-ray diffraction (XRD) was performed to characterize the phase structure and orientation, with copper K_{α} radiations in the $\theta - 2\theta$ configuration. For electrical characterization, two configurations were used on oxidized silicon substrates: (i) Hall bars and (ii) squares patterned by lift-off on the same substrate. This way, both structures were deposited at the same time on the same substrate, guaranteeing that they have the same properties. The Hall bars were used for fourprobe measurements (Keithley 2400), while four-point bending of the substrate was performed to measure piezoresistance. To extract charge

O ₂ /(Ar+O ₂) [%]	20	27	33	40	47	53	60	66
h_f (on SiO ₂) [nm]	136	148	150	149	121	139	192	178
v _{dep} [nm/min]	19.3	16.7	15.0	6.0	3.2	2.3	2.2	2.0
\mathbf{h}_f (on glass) [nm]	112	119	102	111	117	109	/	/

Table 4.1: Thickness of the samples deposited on oxidized silicon substrates (t_{SiO_2}) used for the internal stress and electrical measurements, and on the glass substrates (t_{Glass}) used for the optical characterization.

carrier density and mobility, measurements were done on the squares under a 0.55 T magnetic field (permanent magnet) in the van der Pauw geometry, with HMS-3000 from Microworld. Finally, chemical composition of the films was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Varian 720ES, after being dissolved in an acidic solution, with an estimated error of 3%.

4.2 Results and discussion

4.2.1 Reactive sputtering

There are three possible regimes in reactive sputtering: metallic, transition and oxidized. These different modes can be observed when the discharge voltage (voltage applied between the target and the chamber, the substrate is floating) is measured as a function of the oxygen partial pressure with a fixed current as shown in Figure 4.1a. In addition to the voltage, the deposition rate is measured in-situ with a quartz microbalance. Total pressure also has an influence on the micro-structure so we worked at relatively low pressure $(2.7 \times 10^{-3} \text{ mbar})$ to obtain a compact structure. Some tests at higher pressure showed a microstructure with increased porosity, presumably decreasing the electro-mechanical properties and the focus was thus placed on ZnO deposited at 2.7×10^{-3} mbar. In addition, the lower the pressure, the more we can vary the oxygen concentration while staying in the transition zone, which is interesting to change the type and concentration of defects.



Figure 4.1: (a) Discharge voltage as a function of the oxygen concentration in the chamber, for different total pressures, with a current of 100 mA. The total flow $(O_2 + Ar)$ is kept constant at 30 sccm. The voltage has a first plateau corresponding to the metallic mode of the reactive sputtering. Then a peak appears, corresponding to adsorbed oxygen on a metallic target. The target then gradually oxidizes to reach the poisoned state in a second plateau where the target surface is completely oxidized. (b) Deposition rate per unit of power as a function of the oxygen concentration, measured in-situ with a quartz micro-balance. Three plateaus are observed corresponding to the metallic regime, the transition regime with adsorbed oxygen, and the poisoned regime. The arbitrary units in the graph are different for every curves. (Inset) Average deposition rate measured ex-situ on the different samples.

In Figure 4.1a, the metallic mode corresponds to the first plateau (<13% O₂, discharge voltage V_M =493 V for 2.7×10⁻³ mbar), while the oxidized mode corresponds to the second plateau (>45% O₂, discharge voltage V_O =345 V for 2.7 × 10⁻³ mbar). It can be seen that the transition mode is not a monotonic decrease from V_M to V_O but first has an increase in voltage between 13 and 18%. This increase is due to a layer of oxygen that chemisorbs at the surface of the target and reduces the ion-induced secondary electron emission (ISEE) coefficient, increasing the absolute voltage. [112] When more oxygen is introduced, the target becomes more and more oxidized and ends up completely oxidized. The absolute voltage is then lower than in the metallic mode because the ISEE of ZnO is higher than the one of Zn. [137] When the oxygen flow was increased and then decreased again, no hysteresis in the discharge voltage was observed. This can be explained by the high pumping speed and the small size of the target. [112]

When the oxygen concentration is changed, the deposition rate changes a lot for several reasons such as the state of the target and the voltage. If every other parameter is kept constant, the deposition rate is roughly proportional to the power injected in the plasma. When the voltage drops, the power drops proportionally since the current is here kept constant. To extract the other effects, we plot the deposition rate per unit of power as a function of the oxygen concentration.

In Figure 4.1b we can clearly see that there are three plateaus, corresponding to the metallic, transition and oxidized modes instead of two plateaus like for the voltage. This tends to show that the deposition rate is mainly determined by the state of the surface of the target, as already stated in [106]. The first, second and third plateaus thus correspond to a clean metallic surface, a partially oxidized target with oxygen chemisorbed, and a completely oxidized surface. The initial increase between 0 and 3% O_2 can not be explained by the state of the target surface. Instead, we attribute it to a constant sputtering rate (same amount of zinc deposited) and an increased oxidation of the deposited zinc. Zn and O have a molar weight of 65.4, and 16 g/mol, respectively. For a same amount of Zn deposited, ZnO is thus 24% heavier than Zn, which explains this increase in the few first percent's when the deposit

goes from zinc to zinc oxide. The decrease of the measured deposition rate between ZnO and Zn is lower than the expected 24% because the Z Ratio of Zn (0.514) is lower than the one of ZnO (0.556) [138], making the microbalance overestimating the deposition rate of pure Zn of 8%. [139] The combination of the two effects corresponds to the ~15% increase in deposition rate observed between 0 and 3% oxygen.

4.2.2 Internal stress

There are different origins for stress in thin films and they can be grouped in two families: growth induced and thermal stress. In "growth induced" we include all the origins of stress that occur during deposition, such as epitaxy, or due to defects such as dislocations, point defects, grain boundaries, etc. In thin films there can be a thermal stress even if no intentional heating of the substrate is performed only because the energy of the particles or radiations from the material source heat the substrate, sometimes over 100°C. A thermocouple is used in the chamber to monitor the temperature but since it is not in direct contact with the sample, it could measure a constant temperature even if the sample heats during the deposition. The in-situ stress measurement can thus be used to see if there is any cooling after the end of the deposition. indicating that the temperature increased during deposition. Thermal linear expansion coefficient of silicon is 2.6×10^{-6} K⁻¹ [140] and $4.3 \times$ 10^{-6} K⁻¹ for ZnO [141], leading to a stress of $E_{ZnO}/(1-\nu_{ZnO}) \times \Delta \alpha =$ 0.3 MPa/K, with $E_{ZnO} = 110$ GPa [142] and $\nu_{ZnO} = 0.363$. [143] No variation of stress was measured after the deposition and since the error on the stress measurement is evaluated at 0.6 MPa, the variation of temperature due to the deposition would be a few Kelvin at most. Since no thermal stress is observed, we can assume that all the stress comes from film growth.

The chemical composition had no significant difference according to the ICP-OES. However, this technique does not quantify the oxygen and has a 3% error on zinc. Small changes of stoichiometry are present and have consequences on the optical and electrical properties, and on the internal stress, but are not detected by ICP-OES. XRD confirmed that all the

films are ZnO with a wurtzite structure, and a strong (0002) texture with the c-axis oriented perpendicularly to the substrate surface. No other peak was observed, showing that the defects present in the films are not agglomerated in another phase. Ab-initio studies have shown that different point defects will locally strain the lattice in different ways depending on the type of defect. [45] For instance, oxygen vacancies create tensile stress while interstitial oxygen atoms create compression, which could explain part of the tension for the samples deposited in the metallic mode, and compression for the samples deposited in the oxidized mode.

Another fact to take into account is that the melting temperature of zinc is much lower than the one of zinc oxide. The homologous temperature (T/T_{melt}) during deposition is 0.43 for Zn and 0.13 for ZnO. When Zn atoms reach the substrate, they will thus have a high mobility until they react with oxygen to form ZnO and then have a very low mobility. In the metallic mode, the sample is slightly under stoichiometric, meaning that the atoms have more time to move at the surface before being oxidized, and some atoms remain non-oxidized. There are typically four steps in the stress formation during deposition of a thin film by sputtering, as shown in Figure 4.2. First there is nucleation of the layer, creating compression due to interface effects. Second, there is coalescence and the "zipping" phenomenon creates tensile stress. Third, there is a columnar growth that propagates the tensile stress into the whole film by epitaxy (cross-section visible in Figure 4.3).

Eventually, there can be a decrease of the stress due to atoms diffusing to the grain boundaries. This diffusion to decrease the stress can occur in the bulk and/or at the surface. If it occurs in the bulk, there will be stress relaxation in the whole film over time. If it occurs at the surface, the stress is only decreased locally at the surface during growth, inducing a stress gradient in the film. The samples studied in this article did not show any stress relaxation after deposition meaning that the diffusion of atoms is significant only at the surface. In this situation, the derivative of the stress×thickness curves in Figure 4.4a, σ_{incr} , gives the stress profile in the film. To evaluate stress relaxation in short term, curvature measurements were continued originally on some samples for



Figure 4.2: The four typical steps in the growth of a ZnO thin film deposited by sputtering. (a) Nucleation of the grains that are in compression due to surface stress effects. (b) Coalescence of the crystallites generates tension. (c) Columnar growth of the film with tensile stress imposed by epitaxy. (d) Relaxation of the stress due to incorporation of extra atoms at the grain boundaries.



Figure 4.3: Typical cross section of ZnO thin film deposited on 300 nm of silicon oxide at room temperature at 33% oxygen, showing a columnar growth. No substantial difference was observed with SEM between the samples deposited at various oxygen concentrations.



Figure 4.4: (a) Evolution of the product Stress× Thickness as a function of the deposited thickness, for different oxygen concentrations, monitored with the MOSS technique. The slope of these curves corresponds to the incremental stress. (b) Average stress in ZnO thin films deposited by magnetron DC reactive sputtering at 2.7×10^{-3} mbar in a mixture of Ar and O₂, as a function of oxygen concentration in the chamber.

6 hours after deposition, and no variation was measured on that time scale. As to any long term relaxation, we already reported elsewhere (see Ref. [142]) a technique where ZnO beams were released from the substrate and put under tensile stress, from zero stress up to fracture. With this technique, we did not observe any variation of the stressstrain curve over several months. If stress relaxation is not present in free-standing thin films, we can reliably assume it is not present in thin films deposited on a substrate.

Another important source of stress in thin films deposited by sputtering is the peening. When the particles are sputtered and land on the sample with high energy, the impacts create compression. If the particles experience a lot of collisions before reaching the sample, their kinetic energy will be redistributed and impact the sample with less energy, inducing less compression. The lower the pressure, the lesser collisions there are, and the higher the compression is. In this case, the pressure is quite low $(2.7 \times 10^{-3} \text{ mbar})$, so the peening effect can be important and reach more than 1 GPa in compression, as observed here and in the literature. [144–146]

Above 50% oxygen, the high compressive stress can be explained by peening and incorporation of interstitial oxygen. Because the target is completely oxidized in this regime, most atoms reaching the sample are oxidized and only a few of them are in a metallic state with high mobility. A higher compressive stress could result from a faster oxidation of zinc atoms on the sample surface that limits the diffusion necessary to suppress the defects that create compression. To confirm this hypothesis, we can see in Figure 4.4a that the samples deposited at 47, 53, 60 and 67% O₂ are superimposed up to 20 nm, then a stress gradient reduces the compression. The less oxygen there is, the higher the decrease of compression. Zipping creates some tension in these samples but only for the first 5 nm, before being outmatched by peening. For the samples deposited in the metallic regime, mainly zinc atoms are sputtered and are oxidized on the sample surface. In this situation, peening has less importance since the atoms have a higher mobility to suppress defects. The zipping effect becomes dominant and some tension appears. The curves of the samples deposited at 20, 27 and 33% are superimposed for the first 30 nm, then a stress gradient reduces the tension. The stress gradient is again stronger for samples deposited at lower oxygen concentration. The sample deposited at 20% especially shows an almost zero incremental stress after 50 nm, indicating the presence of non-oxidized Zn atoms that have a high mobility, as it will be confirmed by other characterization techniques further in this article. The deposit at 40% oxygen is in an intermediate situation, resulting in almost zero stress.

4.2.3 Electronic properties

Electrical measurements realized in the van der Pauw geometry give charge carrier density and mobility, and the electrical resistivity as shown in Figure 4.5. No intentional doping was done, meaning that the observed conductivity comes from intrinsic doping. The samples deposited with more than 40% oxygen were in the oxidized regime, leading to a very low charge carrier density and high resistivity that we could not measure with our equipment. At 40%, the resistivity could be measured but the charge mobility and density could not be extracted. We can see that the number of charge carriers increases continuously when the oxygen concentration is decreased. This has a drastic effect on the resistivity for the samples deposited at 40% and more oxygen, where the charge carrier density was too low to be measurable. When the oxygen concentration is decreased from 27 to 20% oxygen however, a saturation of the charge carrier density is observed meaning that the additional defects created by the low oxygen concentration do not participate to the conduction. These additional defects for the sample deposited at 20% however impact the resistivity since they decrease the mobility compared with the sample deposited at 27% oxygen. These electrical measurements have been performed again 17 months later and no significant variation was observed, demonstrating a good stability. The samples were kept at room temperature in ambient atmosphere.

As shown in previous section, the variation of the oxygen concentration induces a variation of stress. Contrary to what has been observed in a previous article [87], no maximum of mobility is observed at the minimum of stress, suggesting that the mobility is controlled by the number



Figure 4.5: Charge carrier density and mobility (a), and resistivity (b) obtained by Hall measurements on ZnO thin films as a function of the oxygen concentration in the chamber during deposition.

and type of defects rather than by the stress. To see if this stress has a significant effect on the electrical properties, piezoresistance measurements were done, measuring the resistivity of the samples as a function of their deformation, imposed by bending of the substrate. This strain is added to the initial strain due to the deposition and can be seen in Figure 4.6.

With the piezoresistance measurement done on a substrate in flexion, we obtained a gauge factor $(\Delta R/R)/\varepsilon$ of -6.1, -5.8 and -8.5 for the samples deposited at 20, 27 and 33% oxygen, respectively, which is in the same order of magnitude as reported in the literature. [130] As shown in Figure 4.6b, the variation of resistance only due to the strain is way too small to explain the variation of resistivity between the different samples. The defects in the samples due to the variation of oxygen concentration are here clearly dominant over the effect of the deformation.

4.2.4 Optical properties

The defects present in ZnO strongly influence the optical properties since they create energy levels inside the bandgap, allowing absorption at energies (wavelength) smaller (larger) than the bandgap of pure ZnO. ZnO thin films have been deposited on glass substrates in the same conditions as the samples deposited on oxidized silicon substrates to perform transmission and reflection measurements (see Figure 4.7a). We assume that the samples of the two series have similar properties since they were both deposited on amorphous SiO_2 so the different substrates should not have any influence. It can be seen that the transmission drops at around 380 nm and 800 nm correspond to reflection peaks originating from the interferences in the thin film, strongly depending on the film thickness. Based on these results, Transmission Matrix Method (TMM) simulations have been performed to extract the refractive index n, and the extinction coefficient k (see Figure 4.7b,c). The variation of these coefficients (at 450 nm) as a function of oxygen concentration shows that a transition in the refractive index occurs between the metallic and oxidized mode.

The films deposited with less oxygen are less transparent (higher k)



Figure 4.6: (a) Variation of resistivity as a function of an applied strain, obtained by four-contact measurements on bent substrates. (b) Resistivity as a function of the total strain. The blue dots represent the initial strain in the samples due to deposition process. The black lines correspond to the variation of resistivity due to the additional strain applied by bending of the substrate.

as expected for samples with more defects. For the sample deposited with only 20% oxygen, the clear drop in transmittance is due to the increased amount of defects which also decrease the electron mobility. These defects strongly increase the absorbance in the visible spectrum, particularly near the bandgap. As for the resistivity, the optical properties are rather controlled by the number and type of structural defects and not significantly by the stress.

The integrated transmission on the visible spectrum depends on the thickness of the film, due to the absorption that increases with the thickness, but also due to the position of the interferences that favour or not the reflection. To avoid the effect of the interferences, one possibility is to compare the transmission of the samples when there is no reflection (maximum of transmission) due to the interferences. At this precise wavelength we can make the approximation that the absorption $A = 1 - T - R \simeq 1 - T$ can be evaluated only with the transmission spectrum. In this case, it is clear that the sample deposited at 20%oxygen (metallic mode) has lots of defects that absorb light and corresponds to non-stoichiometric ZnO. Between 27 and 40% (transition mode) the transmission increases with the oxygen, indicating that the concentration in defects decreases even if the films are still not completely stoichiometric. From 47% and more, there is a saturation of the maximal transmission at 99.4% of the incident light, corresponding to stoichiometric ZnO in agreement with the electrical measurements. The transmission measurements showed no significant variation over a period of 17 months.

With the absorbance it is possible to calculate the optical bandgap thanks to the transition between "absorbent" and "transparent" visible on a Tauc plot. However, the interferences cause imprecisions if the absorption is only calculated based on the transmission because what is interpreted as a transition from "transparent" to "absorbent" is actually a transition from "transparent" to "reflective" which does not allow the calculation of the bandgap. The absorbance must thus be calculated based on the transmission and reflection spectra as shown in reflected based on the transmission and reflection spectra as shown in reflective [105]. Here the optical bandgap is 3.27 ± 0.04 eV, with the observed variation mainly due to imprecisions caused by the position of



Figure 4.7: (a) Transmission and reflection spectra of the glass substrate and of the substrate with ZnO films, for different oxygen concentrations during deposition. Experimental curves are plotted in solid lines and simulations in dashed line. (b) n and (c) k index of the materials, obtained by simulations to fit the experimental curves. The insets show n and k at 450 nm as a function of the oxygen concentration during deposition. (d) Integrated relative transmission $\int_{vis} T/T_{sub} d\lambda$, and maximum of the relative transmission, as a function of the oxygen concentration during deposition.

interferences and not significantly to the stress or the oxygen concentration. The fact that there is no shift of the bandgap with the number of charge carrier (Burstein-Moss effect) indicates that even at low oxygen concentration the doping is still not sufficient to obtain a degenerate semi-conductor. [147]

4.3 Conclusion

Oxygen concentration in the Ar/O_2 plasma is of utmost importance during reactive sputtering of zinc oxide because it changes the stoichiometry. We studied the effect of this variation of stoichiometry on the growth mechanisms and internal stress thanks to a Multi-beam Optical Stress Sensor (MOSS). The average stress is in tension for the samples deposited in the transition regime (up to 340 MPa), and in compression for the samples deposited in the oxidized regime (down to -1.14 GPa). All the samples exhibit a strong (0002) texture according to XRD.

As expected, stoichiometric ZnO (deposited in the oxidized regime) is electrically insulating. When ZnO is deposited with lower oxygen concentration (transition mode), more defects are introduced, intrinsic doping becomes significant and the resistivity drops down to $4 \times 10^{-2} \Omega$.cm. When the oxygen concentration is too low, the resistivity rises again because the high amount of defects decreases the electronic mobility without increasing the effective concentration in charge carriers. This sample with low oxygen also exhibits a drop in transmittance. When oxygen concentration is increased, the thin films are more and more transparent and reach a plateau in the oxidized regime.

The fact that the electric conductivity comes from the same defects that limit the transmission makes iZnO unsuitable for transparent electrodes. Indeed, it is therefore not possible to have a sample with both a high conductivity and high transparency. If we estimate the figure of merit defined in equation 1.3 ($\phi = 1/R_s \ln\left(\frac{1}{T_{\text{max}}}\right)$), we find that the maximum is obtained with 20% oxygen where $\phi = 1.8 \cdot 10^{-3}$. At the beginning of the oxidized regime it drops to $1.5 \cdot 10^{-5}$. These values are much lower than what can be obtained with AZO as it will be shown in Chapter 5. We studied piezoresistance by bending of the substrate and showed that the internal stress does not have a significant effect on resistivity. Gauge factor was measured around -6 in the transition regime and reached -8.5 for the sample near the oxidized regime. For applications in transparent and flexible electronics, when room temperature deposition is needed, ZnO deposited by reactive sputtering can thus be a good candidate. Its gauge factor (6-8) is lower than other usual semiconductors deposited at higher temperatures (up to several hundreds), but higher than metals (2-3), and is transparent contrary to metals and small bandgap semiconductors.

The optimal conditions for piezoresistors according this study are corresponding to the very end of the transition regime $(2.7 \times 10^{-3} \text{ mbar}, 33\% \text{ oxygen})$, where resistivity is high but still easily measurable, and the optical transmission is high: $\max(T/T_{sub} > 95\%)$. The different stress origins are balanced and almost zero stress is obtained, which limits the risks of premature fracture. In addition, these conditions correspond to the highest gauge factor.

Chapter 5

Sputtering of AZO

As seen in Chapter 4, the optical and electrical properties of zinc oxide can be largely tuned by changing the oxygen concentration in the chamber during the reactive sputtering, hence changing the stoichiometry. This way of tuning the properties is however not the best for several reasons, due to the fact that the conductivity mainly comes from nonoxidized zinc atoms:

- The metallic zinc atoms absorb light. To have a transparent intrinsic ZnO (iZnO) thin film, it must therefore be completely oxidized and is then insulating.
- To reach the highest conductivity, lots of defects must be present (oxygen vacancy and/or zinc interstitials), which limits the mobility to 6 cm²/V.s in our experiments, for a resistivity of $4 \cdot 10^{-2}$ Ω .cm.
- It is impossible to have the highest transparency and conductivity at the same time. If an application requires high transparency, we must therefore work near the oxidized regime, where the resistivity can vary of several orders of magnitude, leading to a very unstable process. If a high conductivity is needed, we need to work near the metallic regime, leading to a process with an unstable transparency.

• Even though a stability at room temperature was observed for electrical, optical, and mechanical properties, non-oxidized zinc is intrinsically not stable and tends to oxidize over time. At high temperature especially, non-stoichiometric ZnO gets oxidized over time and becomes insulating.

For all these reasons, iZnO is a bad choice for transparent conductive layers. As for every semi-conductor, it is much more preferable to dope it to obtain an increased conductivity. Different dopants are possible as discussed in Chapter 2. Aluminum has been chosen in this work because it is the most used, is a non-toxic, abundant and cheap metal. To have a continuity with the study of iZnO, the oxygen concentration is the parameter that has been mainly studied.

5.1 Experimental method and studied parameters

The methods used to deposit and characterize are essentially the same as the ones used for the iZnO thin films. The deposition was done by DC reactive sputtering and the characterization techniques used are the MOSS, SEM, XRD, spectrophotometry, ICP-OES, Hall and piezoresistance measurements. For more details about the experimental methods, please refer to section 4.1 and chapter 3. This section focuses on the explanation of the different parameters that are studied about AZO, and the different types of samples that were prepared for these purposes.

Annealings have been studied for AZO and not for iZnO because in iZnO, annealings decrease the concentration of defects and make the material insulating, hence useless for transparent electrodes. For AZO, an annealing does not remove the extrinsic dopants and can even activate them. An annealing can also increase the electronic mobility by decreasing the defects concentration.

To limit the studied factors to oxygen concentration and temperature, the target always had the same composition: Zn(98.68)Al(1.32) with a purity of 99.99%. A compound target was preferred over co-sputtering with Zn and Al targets because of the better control over the ratio Zn/Al.

Indeed, in co-sputtering it would not be possible to independently control the atmosphere of each target, leading to targets in different regimes. In addition, a doping level on the order of 1% is difficult to achieve accurately because the deposition rate of aluminum should be on the order of two orders of magnitude lower than the deposition rate of zinc. This would require a very low applied current on the aluminum target, which could lead to instabilities of the plasma. Finally, co-deposition can lead to cross-contamination of the different targets.

As for iZnO, the discharge curve has been measured to identify the metallic, transition and oxidized regimes. This was done only at 2 mTorr, since it has been shown with iZnO that increasing the pressure increases porosity. With pressures lower than 2 mTorr, some instabilities could appear for lower power. Different series of samples were produced on different substrates, with different designs, to extract different properties, as a function of temperature and oxygen concentration.

1) Influence of oxygen concentration

Three different series of samples were produced as a function of oxygen.

This first series of samples (named **AZO O**) was deposited on different types of substrates, with a constant current (125 mA), total pressure (2 mTorr), at room temperature, and the oxygen concentration was varied (10, 15, 20, 25, 30, 35, then 17.5, and finally 22.5% oxygen). The chronological order of the depositions is important because there is a drift while using the target. The samples deposited at 17.5 and 22.5% oxygen therefore do not fit well with the others and appear slightly as outsiders. Three types of substrates were used and were disposed as shown in Figure 5.1 during deposition. These substrates had different purposes:

• Oxidized silicon wafer. This type of substrate was placed in the center of the sample holder to allow the measurement of the curvature with the MOSS. Glass was avoided here because a substrate with a low reflectance can lead to low signal. The silicon was oxidized to allow electrical measurements on the deposited thin films.

- Glass. These substrates were used for XRD, optical transmission, and electrical measurement (Hall measurements in Van der Pauw geometry). Optical reflection could not be measured on these samples because the minimum size required by our equipment for these measurements is 2.5x2.5 cm². These samples were also used for the annealings. Annealings were performed for 15 min under argon at 100, 200, 300, 400, 500, 600, and then 700°C, on the same piece of sample each time. After each annealing, the optical transmission and electrical properties were measured.
- Silicon. These substrates were used to have a conductive substrate to obtain high resolution images of cross sections in the SEM. They were also used to measure the composition of the films by ICP. Indeed, Si is not dissolved in HF contrary to AZO, allowing a selective etching and avoiding contamination by the substrate.

A second series of samples was produced to characterize AZO near around the transition regime (13%, 18%, 23% and 28%). For these samples, the Lab-On-Chip design (named **LOC AZO**) has been chosen to combine electrical and mechanical characterization. This series was deposited with a new target, in contrast to the AZO O and AZO Tseries that were deposited with an eroded target (see section 5.2 for more information). The samples were deposited at room temperature since heating would damage the photo-resist used for the lift-off, the current was fixed at 100 mA and the pressure at 2 mTorr. These samples are three inches wafers containing different parts allowing different characterizations:

- Twelve identical chips that contain :
 - Structures to measure the mismatch.
 - Structures to measure the stress-strain curve.
 - A square of AZO on oxidized silicon to measure the resistivity, and the charge carrier mobility and density in the Van der Pauw geometry.

– A square of $1 \times 1 \ mm^2$ of AZO directly on silicon used for nano-indentation.

Several of these chips were annealed at 300, 400, 500, and 700°C, for 15 min under argon. Note that in this case each annealing was performed on different instances, contrary to the samples of the AZO O series where the annealings were performed successively on the same piece of sample.

• A 2x2 cm² square of AZO deposited directly on silicon for in-situ curvature measurements.

Only parts of the results on *LOC AZO* are presented here to study the effect of the erosion of the target. The complete results are shown in Chapter 6 that focuses on the lab-on-chip technique. These samples are however also mentioned in this chapter because part of the chips are simple annealed thin films used for the characterization of the electrical properties, and not of the stress-strain curve that is the main objective of the lab-on-chip technique as it will be discussed in Chapter 6.

Finally, a third series of samples was deposited on 3 inches oxidized silicon substrates, with Hall bars patterned in the center of the substrates. These larger samples were used in a bending equipment to extract the piezoresistive coefficients. Three samples were produced, in the metallic (10%), transition (17.5%), and oxidized (30%) regimes.

2) Influence of temperature (AZO T)

This series was done on the same types of substrates as the samples from series AZO O. AZO O was used to observe the effect of oxygen concentration and post-deposition annealings. However, the effect of temperature is more important during deposition than during an annealing because it increases the mobility of particles at a free surface, while a post-deposition annealing increases the mobility of atoms embedded in a 3-D lattice. The different depositions were done at temperatures of 20, 60, 100, 140, 180, and 220 °C. Higher temperatures were not studied because the vapor pressure of zinc becomes high, limiting the deposition



Figure 5.1: Different types of substrates used for preleminary characterization of AZO. The substrate holder holds five square substrates : two glass substrates $(1.25 \times 1.25 \text{ cm}^2, \text{ thickness } 500 \ \mu\text{m})$, two silicon substrates $(1.25 \times 1.25 \text{ cm}^2, \text{ thickness } 380 \ \mu\text{m})$, and an oxidized silicon substrate $(2.5 \times 2.5 \text{ cm}^2, \text{ thickness } 380 \ \mu\text{m} \text{ with } 300 \ \text{nm } SiO_2)$.

rate because of the re-evaporation of zinc atoms. The oxygen partial pressure was fixed at 20%, around the center of the transition regime, because the properties were the most interesting (high transparency and conductivity), and this regime is the most sensitive to a change of the experimental conditions. The drawback is that they were also more sensitive to the drift due to the erosion of the target. The current was fixed to 125 mA, and the total pressure to 2 mTorr, like for series AZO O.

5.2 Target calibration

As said previously, two targets were used for the AZO depositions and will be referred to as "eroded target" and "new target". They have the same composition ($Zn_{98.68}Al_{1.32}$), but the eroded target was strongly eroded during the experiments presented here while the new target had a planar surface. Like for the Zn target, a discharge curve has been measured and is shown in Figure 5.2. A comparison between the new and eroded Zn:Al targets is also presented, along with the discharges curves of the Zn target at two different erosion states.

In the discharge curve of the Zn target, three regimes were observed: metallic, transition and oxidized. At the beginning of the transition regime, an increase of the voltage was observed and is attributed to the adsorption of oxygen at the surface of the target. Under this adsorbed layer, the zinc is mainly non-oxidized between 15 and 35% oxygen. This corresponds to a plateau in the deposition rate. Between 35 and 45% of oxygen, the deposition rate drops from around 60 to 20 [a.u.] and the voltage decreases slightly faster before reaching the oxidized regime. We interpret this second part of the transition regime as the adsorbed layer of oxygen being replaced by an oxide layer at the surface of the target. For the discharge curve of the Zn:Al target, some conclusions are still valid:

• In the metallic mode, the voltage is constant. There is a plateau in the deposition rate, corresponding to a non-oxidized target and under-stoichiometric AZO.



Figure 5.2: (Top) Discharge voltage and deposition rate measured in-situ with the micro-balance, as a function of oxygen concentration in the plasma during sputtering, at 2 mTorr, with a current of 100 and 125 mA for the Zn and Zn:Al targets respectively.

(Middle) Comparison between the discharge curves of the Zn target at two different erosion states with a current fixed at 100 mA, and a total pressure of 2 mTorr.

(Bottom) Comparison between the discharge curves of the eroded and new targets of Zn:Al with a current fixed at 125 mA and 100 mA, respectively.

- The initial increase of the deposition rate between 0 and 3% of oxygen corresponds to deposition of Zn (Zn:Al), then ZnO (AZO), that is heavier per mole of Zn (Zn:Al) deposited.
- There is a plateau in the deposition rate and voltage at higher oxygen levels corresponding to an oxidized target and deposited material.
- The slow decrease of deposition rate in the oxidized regime is due to the decrease of the partial pressure of argon, replaced by oxygen that has a lower sputtering yield.

The transition regime is however different for the Zn:Al target than for the Zn one. The voltage and the deposition rate have a smoother, monotonic decrease from the metallic to the oxidized regime. We believe this is due to the small presence of aluminum. Indeed, aluminum has a high affinity with oxygen. When oxygen arrives on the target, it will thus react to form an oxide layer instead of being adsorbed. Therefore, we do not observe the peak of voltage at the beginning of the transition zone anymore, nor a plateau in the deposition rate, which were both due to adsorbed oxygen. Aluminum in reactive sputtering is also known to have a brutal transition from the metallic to the oxidized regime for the same reason. This is the reason why the transition regime is here narrower for Zn:Al (10-30%) than for Zn (12-45%).

Figure 5.2 also shows the discharge curves for an eroded and a new target, for Zn and Zn:Al targets. Note that in order to have similar deposition rates, different currents have been used in the case of Zn:Al (125 mA for the eroded one, and 100 mA for the new one). In magnetron sputtering, the erosion of the target is highly heterogeneous due to the magnetic field that confines the plasma. It means that when the target gets eroded, it is not plane anymore and the area of the target increases. At a constant current, the density of current is thus decreased. If the density of current is decreased, the erosion rate of the target is decreased too, and there is more time for oxygen to oxidize the surface of the target. It means that the transition zone will be shifted toward lower oxygen concentrations when the density of current is decreased. It is

indeed what we observe here since the transition zone is shifted to lower oxygen concentrations of 2 and 1.5% for the more errored Zn and Zn:Al targets, respectively. It means that for the Zn:Al target, increasing the current from 100 mA (new target) to 125 mA (eroded target), is still not sufficient to maintain the current density. The variation of voltage at low oxygen concentration could be explained by the same mechanism: an increased surface means a decreased current density, hence the lower voltage. Although this explanation considering only the current density is consistent with our experiments, it is a simplification of reality. In reality, the erosion of the target and the emission of the sputtered particles is angle dependent as shown in Ref. [148]. When the target is eroded, it would be necessary to take into account the variation of the inclination of the surface to have a rigorous explanation.

At higher oxygen concentration (66%), the voltage converges to approximately 350 V, independently of the erosion state or the aluminum doping of the target. This is confirmed for the Zn:Al target, as depicted in Figure 5.3, where the discharge voltage has been measured as a function of the current, on the new target. Since this experiment was short, we can consider the erosion state as constant in the experiment. Hence, changing the current is equivalent to changing the current density only for this experiment. For the metallic mode, the voltage drops from 587 (new) to 517 V (eroded target) which corresponds to a decrease of the current density around 33% (Fig. 5.3) while the current was actually 25% higher for the eroded target. Combining these, we can conclude that for the same current, the current density is decreased by approximately 50% when the target goes from new to highly eroded.

In Fig. 5.3, the deposition rate appears as linear with the current at 0 and 66% oxygen. This is logical since the state of the target does not change with the current (metallic and oxidized respectively). In this case, the current is proportional to the impacting ions, hence the sputtering and deposition rate. In the transition regime the situation is different: an equilibrium is reached between oxidation of the target by the oxygen, and sputtering of the oxide layer by the argon ions. This equilibrium determines the oxidized fraction of the target and the deposition rate. When the current is increased, the erosion rate increases


Figure 5.3: Discharge voltage (Top) and deposition rate measured in-situ (Bottom), as a function of the sputtering current, in the metallic regime (0% oxygen), transition regime (22.5%) and oxidized regime (66%). The total pressure is 2 mTorr and the total flow $(Ar+O_2)$ is 30 sccm.

and the oxygen has less time to oxidize the surface of the target (lower oxidized fraction). This explains why at 22.5% of oxygen, it goes from the oxidized to the metallic mode when the current is increased.

5.3 As deposited characterization

5.3.1 Structural characterization

Two techniques were used to characterize the micro-structure of the AZO films, scanning electron microscopy (SEM) and X-Ray diffraction

$O_2/(Ar+O_2)$ [%]		10	15	17.5	20	22.	5 2	5	30	35
t [nm] 34		343	347	346	337	36	8 33	33	339	384
v _{dep} [nm/min] 23		23.2	20.5	16.4	16.7	9.5	5 10	0.0	7.3	6.3
	$\begin{array}{c c} T_{Dep} [^{\circ}C] \\ t [nm] \end{array}$		20	60	100	140	180	22	0	
			328	334	325	328	355	35	5	
$v_{dep} \ [nm/min]$		11.1	9.7	9.0	7.7	5.3	3.4	4		

Table 5.1: (Top) Thickness measured by SEM for samples deposited at various oxygen concentrations (room temperature), and (Bottom) at various temperatures (20% oxygen), with a total pressure of 2 mTorr and a current of 125 mA.

(XRD). SEM gives information about the size of the grains, their shape, the thickness and the roughness of the film. However, it does not give information about the texture (crystal orientation). XRD gives information about the crystalinity, and can also give information about texture and grain size. However, as discussed in section 3.1, all these information depend strongly on the position of the sample during the measurement, which is not very accurate in our equipment. SEM images of the AZO thin films are presented in figure 5.4, for films deposited at various oxygen concentrations, different deposition temperatures, and different annealing temperatures. From these images, the thicknesses have been measured and are presented in table 5.1.

As shown in Fig. 5.4, the sample deposited at room temperature and 10% oxygen exhibits a heterogeneous aspect over the thickness. The first tens of nanometers seem to contain smaller grains, and are followed by an approximately columnar growth resulting in larger grains at the top of the layer. Quantitative analysis would however require TEM images because the structure of the nucleation layer is not clearly visible with SEM. This structure indicates that the sputtered atoms have a mobility large enough to have grain growth as the thickness increases. When the oxygen concentration is increased, the mobility of deposited atoms decreases because of the faster oxidation.

In a first approximation, metallic zinc atoms at the surface can be considered as mobile because of their high homologous temperature $(T/T_m=0.43)$, while oxidized zinc atoms can be considered as immobile $(T/T_m=0.13)$. If the mobility of sputtered atoms is decreased, nucleation of only small grains is possible, followed by a columnar growth without grain growth. The columns hence have the same width over the whole film, without an apparent nucleation layer. A transition can be observed between 25 and 30% oxygen (corresponding to the end of the transition regime and the beginning of the oxidized regime), going from irregular columns on top of a nucleation layer, to sharp columns homogeneous over the whole thickness.

Increasing the temperature has an effect opposite to increasing the oxygen concentration, since a higher temperature corresponds to a higher mobility for the sputtered atoms. A deposition temperature of 220°C corresponds to an homologous temperature of 0.71 for zinc, leading to zone 3 in the Thornton structural zone model. It is indeed observed in this work. As the deposition temperature is increased from room temperature to 220°C, the width of the columns increases, and eventually the grain boundaries are not clearly visible anymore, as the film recrystallizes. Atoms have a high mobility at such low temperatures because they are deposited on a free surface and not immediately oxidized during the reactive sputtering.

When the deposition is finished, the atoms are embedded in a 3-D lattice and mostly oxidized so they have a much lower mobility than during deposition. The effect of temperature during an annealing is also presented in Fig. 5.4, for RTA of 15 min under argon atmosphere. A similar trend is clearly observed, for much higher temperatures though. This can be explained because the homologous temperature of Zn at 140°C is 0.59. The same homologous temperature for ZnO corresponds to about 1050°C. However, taking the homologous temperature of Zn during deposition, and of ZnO after deposition is a gross approximation that can only be used for qualitative comprehension, not for quantitative prediction.

To characterize the micro-structure, XRD experiments have been done and the resulting scans are presented in Fig. 5.5. Important information



Figure 5.4: SEM images of the cross section of different AZO samples, all at the same magnification. (Top) Deposited at room temperature at different oxygen concentrations. (Middle) Deposited at various temperatures, with 20% oxygen. (Bottom) Pieces of a sample deposited at room temperature, with 20% oxygen, and annealed for 15 min at different temperatures, under argon.

that can be extracted from XRD peaks is their intensity, full width at half maximum (FWHM), and their position. These information are shown for the (002) peak in Fig. 5.6. The (002) peak at 34.5° is the dominant one in ZnO and AZO deposited by sputtering because the spontaneous growth orientation is with the *c*-axis perpendicular to the substrate. Some small other peaks are however visible at 36.3° (101), and 47.3° (102). The other peaks are not identified as ZnO peaks and belong to the background. Zn has a peak at 36.5° that is probably the one observed here for the sample deposited with only 10% oxygen, confirming the presence of metallic clusters, that will be discussed in electrical (section 5.3.3) and optical properties (section 5.3.4). No Al₂O₃ peaks could be observed, meaning that if alumina clusters are present in the AZO films it is in very small concentration, or in an amorphous phase.

Since no other peak than the (002) has a significant intensity, it can be assumed that the intensity of the (002) peak is an indicator of the crystalline fraction in the film. The FWHM can be correlated to the grain size because grain boundaries contain defects that broaden the peaks. However, other defects broaden the peaks too, so the FWHM can be seen as an indicator of the perfection of the grains. The larger the FWMH, the more defects there are, including grain boundaries. The position of the peaks is shifted when a homogeneous strain is applied to a material. A shift to larger angles indicates in-plane tensile stress. [149]

It can be seen in Fig. 5.6 that the intensity of the (002) peak is low for samples deposited in the metallic and transition regime (10-25%), and increases in the oxidized regime (30-35%) where the sharper and more homogeneous grains were observed by SEM. As seen in Fig. 5.4, increasing the deposition temperature has a huge impact on the crystalinity. It is observed here as well, with an increase of two orders of magnitude in the (002) intensity when the deposition temperature is increased from 20 to 220° C. Annealings of the AZO O samples do not seem to have a significant influence over the intensity, except for the sample deposited at the limit between the transition and oxidized regimes (30% oxygen). However, a decrease of the intensity with the annealing seems unlikely. Moreover, all the other minor peaks also have a decreased intensity for



Figure 5.5: XRD scans of AZO samples deposited on glass substrates at various oxygen concentrations (Top and Middle), and at various temperatures (Bottom). The samples deposited at various oxygen concentrations have been scanned as deposited (Top) and after an annealing at 700° C for 15 min under argon atmosphere (Middle). The scans in a same plot are shifted from each other for more clarity.



Figure 5.6: Intensity (Top), full width at half maximum and grain size D (Middle), and position (Bottom) of the (002) peak, for AZO samples deposited at various temperatures (AZO T), and various oxygen concentrations (AZO O). The AZO O samples have been measured as deposited (solid line) and after an annealing at 700°C for 15 min under argon atmosphere (dotted line).

this sample so the apparent decrease due to the annealing is probably a decrease of intensity due to a tilt of the sample during measurement.

With the FWHM, it is possible to evaluate the grain size thanks to equation 3.2. However, other defects than grain boundaries also influence the FWHM. In addition, this formula gives an average value and in the AZO films a nucleation layer with much smaller grains is often present, which can lead to a wrong interpretation. The fact that annealing decreases the FWHM in the transition and oxidized regimes but not in the metallic regime could be explained by a re-crystallization of amorphous grain boundaries for the samples deposited at higher oxygen concentration (Zone T of the Thornton zone model).

As previously said (see section 3.1), the position of the peaks can be used to measure a stress in a thin film, with a large imprecision though. An increase of the diffraction angle means that an in-plane tensile stress is present. The analysis of the position of the (002) peak thus gives contradictory results to what was observed in-situ with the MOSS. The latter technique having a much better accuracy, the stress evaluated by XRD will be considered as not accurate enough with our equipment.

5.3.2 Internal stress

Variation of oxygen concentration

For ZnO, a clear transition was observed between the stress in samples deposited in the transition and the oxidized mode, going from tensile stress (340 MPa) to high compressive stress (-770 MPa) at 33 and 47% of oxygen, respectively. For AZO, this transition was not observed (see Fig. 5.7), and all samples exhibit tensile stress, with a monotonic increase from the end of the metallic regime (10% oxygen, 68 MPa) to the beginning of the oxidized regime (30% oxygen, 497 MPa). Tensile stress is still observed at high oxygen concentration, even though a small decrease appears (50% oxygen, 322 MPa). The stress evolution during growth is shown in Fig. 5.8. For more readability the samples deposited at 17.5% and 22.5% oxygen are not presented, and a smoothed version of the figure is presented in appendix (Fig. A.1). As for ZnO, stress

relaxation is here considered negligible and the derivative of the curves corresponds to the stress profile in the films. All the curves have an almost constant slope after 100 nm. In this situation, the average stress can be characterized by two parameters: the final stress, and the initial gradient. The curvature measurement is very noisy, making its numerical derivative unclear, especially at low thickness. The approximated curves presented in Fig A.1 are smooth enough to be derived and extract the stress profile in the films. Note that as every approximation, it contains errors so the stress profile should be taken as qualitative more than quantitative.

It can be observed that the stress profiles obtained in the transition regime (10-25% oxygen) are similar, except for the first nanometers where the stress gradient increases as the oxygen concentration is increased, resulting in a shift of the stress profile after ~ 25 nm. This could be a phenomenon similar to what was observed for iZnO. When the oxygen concentration is increased the mobility of sputtered atoms is decreased, hence decreasing the presence of adatoms at the grain boundaries. Increasing the oxygen concentration therefore limits the compensation of the zipping effect and the tensile stress increases.

At the beginning of the oxidized regime, the final stress continues to increase (less adatoms to compensate the zipping effect) but the initial gradient extends over a larger range (lower initial stress). This could be due to an initial amorphous matrix between the grains (zone T of Thornton's model) that would be present due to a low mobility of the species. As the film grows the crystalline part would grow, resulting in a denser material. The reduction of the free space would induce tensile stress like the zipping effect. [150] As the oxygen concentration is increased, the amorphous part is present over a larger thickness before crystallizing, resulting in a larger stress gradient and a decreasing average stress.

The decrease at 50% oxygen could also come from the increased presence of alumina clusters as it will be shown in Chapter 6, or the peening effect that would become significant at large oxygen concentration, like for iZnO.



Figure 5.7: (Top) Average stress in two series of AZO thin films, as a function of oxygen concentration in the plasma. The stars indicate that these deposition have been done after all the others, meaning there has been a drift between this part of the curve and the dots. (Bottom) Average stress in the AZO thin films, as a function of the deposition temperature. The stress is shown at the end of deposition (before cooling, at T_{dep}), and after cooling, at room temperature.



Figure 5.8: Evolution of the product Stress× Thickness as a function of the deposited thickness, for different oxygen concentrations (Top), and different deposition temperatures (Bottom). For the samples heated during deposition, the cooling down has been recorded to have the average stress at room-temperature.

Variation of deposition temperature

When the deposition temperature is varied, all the Stress×Thickness curves are linear, with a slope going from tensile to compressive stress when the temperature is increased. When the samples are cooled down this variation of stress is reduced by the thermal stress that is in tension because the thermal expansion coefficient of the substrate (silicon) is lower than the one of AZO.

In reference [87], the decrease of the tensile stress, and apparition of compressive stress is explained by the incorporation of adatoms at grain boundaries that are in tension due to the zipping effect. However, this stress-driven diffusion would only relax the tensile stress and not create compression. [151] When the deposition temperature is increased, the mobility of atoms increases and the zipping effect is more and more counterbalanced by the diffusion to grain boundaries. At 180°C the mobility would be enough to completely cancel the zipping effect.

The compression observed in the sample deposited at 220°C must be explained in another way. During growth, 2-D islands are formed on the surface of the grains, with a usually higher density than the grain boundaries density. The edges of such islands form preferential sites to incorporate extra atoms, inducing compressive stress in the bulk of the grains. [150, 152] Here, the relatively high temperature could also favor the re-evaporation of zinc atoms and the incorporation of extra oxygen, forming Al_2O_3 clusters, as it could be suggested by the electrical measurements (see Section 5.3.3). This would be consistent with the apparition of some compression for the sample deposited at 50% oxygen.

5.3.3 Electronic properties

The main application for AZO is as a conductive layer and deposition temperature has already been demonstrated as an important parameter. [87] Here, we also investigated the effect of oxygen concentration during the reactive sputtering as it was of primal importance on the electronic properties of iZnO.

Variation of oxygen concentration

As for iZnO, the charge carrier in AZO decreases as the oxygen concentration is increased. In the metallic regime, a high charge carrier is present as the film is non-stoichiometric and contains lots of metallic atoms. In the transition regime, a degenerate semi-conductor is deposited with less and less free carriers ($\sim 10^{21} - 10^{20}$ cm⁻³) as the metallic atoms are more and more oxidized. In the oxidized regime the charge carrier drops quickly ($3 \cdot 10^{19}$ and $2 \cdot 10^{18}$ cm⁻³ at 30 and 35% oxygen, respectively).

This drastic drop of charge carrier density could be due to presence of Al₂O₃ clusters instead of Al atoms in substitution. [23] Instead of acting like a dopant, aluminum would then form a second phase, almost inert electrically. This would lead to a material with electrical properties similar to ZnO at the beginning of the oxidized regime $(n \sim 10^{18} - 10^{19} \text{ cm}^{-3}, \rho \sim 10^{-1} - 10^1 \Omega.\text{ cm})$ as observed in Fig 5.9.

Electronic mobility is an indicator of the crystal quality. Here, its maximum is observed for samples deposited with 17.5-20% oxygen. These samples correspond to near-stoichiometry samples since they have a high but not maximal optical transmission. More specifically, they are more absorbent in infrared than oxidized samples, which is a metallic behavior due to the large concentration of free carriers (see section 5.3.4).

As observed in iZnO when oxygen concentration is too low the electronic mobility is decreased due to the presence of defects such as interstitial zinc, or even metallic clusters for AZO deposited with 10% oxygen. On the other hand, too much oxygen induces alumina clusters that decrease the electronic density and mobility. The beginning of the transition regime (17.5-20% oxygen) is therefore an optimum where there is not much interstitial zinc, and aluminum atoms are still in substitution in the lattice instead of forming alumina clusters. In addition, the high carrier density allows an efficient screening of the defects that increases the electronic mobility.



Figure 5.9: Charge carrier density (Top), mobility (Middle), and resistivity (Bottom) of AZO thin films as a function of oxygen concentration. LOC AZO series (red) was done with a new target, meaning that the discharge curve is shifted to the right compared to the AZO series (blue). The stars highlight the samples of the AZO series that have been deposited after the rest of the series, with a more erroded target (shift to the left).

Variation of deposition temperature

A similar study was done in reference [87], where a maximal electronic mobility of 22 cm²/Vs was found at 150°C, with n= $8 \cdot 10^{20}$ cm⁻³, and a resistivity of about $3.5 \cdot 10^{-4}$ Ω.cm. This maximum of mobility was attributed to the minimum of the absolute value of the stress. In the study done here, a similar value of the minimum resistivity is found at 180°C, with a lower charge carrier density ($5.5 \cdot 10^{20}$ cm⁻³) and higher mobility ($31 \text{ cm}^2/\text{Vs}$), as shown in Fig 5.10. Note that the measurement of the resistivity is accurate, while the measurement of charge carrier density/mobility is way more sensitive because it depends on the Hall voltage, which represents a small variation of the transverse voltage when a magnetic field is applied.

What is important here is that the same trend is observed. The maximum mobility is also observed near the minimum of absolute value of the stress (around 200°C), however it was proven in section 4.2.3 that stress has a minimal impact on the resistivity in iZnO, and the same conclusion will be demonstrated in chapter 6 for AZO.

The decrease of resistivity from room temperature to 180 °C can be explained by the decrease of defects such as interstitial Zn and grain boundaries, and activation of aluminum dopants that increase the charge carrier density and mobility. At 220 °C, the resistivity drop could be explained by the apparition of alumina clusters. Indeed, it has been confirmed by ICP that the aluminum concentration increases (see Fig. 5.11) due to re-evaporation of Zn atoms during sputtering. The aluminum atoms that form the alumina clusters can not give a free electron and diffuse the charge carriers, decreasing both charge carrier density and mobility.

The minimum of resistivity is therefore obtained when there is a low amount of point defects and alumina clusters. The minimum of stress observed around the minimum of resistivity is not its cause, but an other consequence of the low amount of defects obtained at this temperature.



Figure 5.10: Resistivity (Top), and charge carrier density and mobility (Bottom) of AZO thin films deposited on glass as a function of deposition temperature.



Figure 5.11: *ICP* analysis of the AZO samples for different deposition temperatures (at 20% oxygen), and different oxygen concentrations (at roomtemperature).

Piezoresistance

As discussed in chapter 4, ZnO thin films could be used as transparent strain gauges. When it is doped with aluminum, its resistivity drops significantly, and a typical application is transparent electrodes, possibly in flexible electronics. In this situation, a lower gauge factor $(\Delta R/R_0/\varepsilon)$ is interesting because the devices need to be as stable as possible with deformation.

Metals have typical gauge factors comprised between 2 and 3. [118–120] For ZnO thin films it was measured around -6 in the middle of the transition regime, and around -8 at the end of the transition regime. The same experiments have been done on AZO samples deposited with 10% (metallic regime), 17.5% (transition regime), and 30% (oxidized regime) oxygen. The results are presented in Fig. 5.12 and correspond to a gauge factor of -1.6, -1.3 and -4.2 for the sample deposited with 10, 17.5 and 30% oxygen, respectively.



Figure 5.12: Relative variation of resistance as a function of strain, for AZO thin films deposited at various oxygen concentrations.

5.3.4 Optical properties

The samples deposited on glass substrates have been analyzed in a spectro-photometer to obtain their transmittance. With the transmittance it is possible to obtain the bandgap using a Tauc plot as shown in section 3.2. The reflectance spectra could not be measured because the samples were too small for our equipment. The transmission spectra are shown in Fig. 5.13 for the samples deposited at various oxygen concentrations (at room temperature) and various temperatures (with 20% oxygen).

It is clear that, as the oxygen concentration is increased, the samples go from a quasi-metallic behavior to a semi-conductor behavior. This is due to the decreased amount of defects, in a similar way as it was observed for iZnO. The sample deposited with only 10% oxygen that exhibits a small Zn peak in the XRD measurements has a very low transmittance, confirming the presence of metallic Zn clusters.

The optical bandgap can be calculated based on the transmission spectra, as explained in section 3.2. As the oxygen concentration is in-



Figure 5.13: Transmission spectra of AZO samples deposited at room temperature for different oxygen concentrations (Top), and at 20% oxygen and different temperatures (Bottom).

creased, the charge carrier density drastically drops. This decrease of the charge carrier density is associated with a decrease of the Fermi level, hence a decrease of the optical bandgap as shown in Fig. 5.14. This is the well-known Burstein-Moss effect that is present in degenerate semiconductors. [153] An extrapolation of the bandgap to n = 0 (iZnO), gives a bandgap of 3.28 eV, consistent with what was observed in section 4.2.4. As the bandgap increases (decreased oxygen), the transmission in the near-UV is enhanced, up to a certain point where a metallic behavior appears.

At 10% oxygen, the absorption due to the metallic clusters becomes too high and the extraction of the bandgap becomes impossible because the sample does not have a semi-conductor behavior anymore. This is why the calculated bandgap of this sample is not shown in Fig. 5.14.

The absorption in the IR spectrum is mainly due to free-carriers and therefore also decreases as the oxygen concentration is increased. The variation of the position of the transmittance peaks is mainly due to variations of the thickness.

When the deposition temperature is increased, the charge carrier density increases up to 180°C then decreases at 220°C. Following the Burstein-Moss effect, the optical bandbap therefore increases with the deposition temperature. At 220°C, a saturation of the optical bandgap is observed as the charge carrier density decreases. This could be explained by the apparition of alumina clusters that trap the charge carriers and decrease the density of state in the conduction band, maintaining an approximately constant Fermi level. However, this should be investigated more deeply since it is based on only one sample and does not follow the same trend as what was observed in Ref. [87].

In the visible spectrum, the transmission is increased with the deposition temperature due to a reduction of the defects, except for the sample deposited at 220°C that is slightly less transparent. Since there is no apparent reason for an increased absorption, a possible explanation would be an increased reflectance and/or diffusion, which we were not able to measure. In the infrared region, the transmission decreases with the deposition temperature due to the increased charge carrier density.



Figure 5.14: (Top) Bandgap as a function of deposition temperature (at 20% oxygen) and oxygen concentration (at room temperature). (Bottom) Evolution of the optical bandgap with the charge carrier density. The bandgap of the sample deposited at 10% oxygen is not represented because its quasi-metalic behaviour makes it invalid.

5.4 Post-deposition annealing

It has been demonstrated that heating the substrate during deposition allows to obtain samples with a better crystallinity, electrical conductivity and optical transparency. However, it is not always possible to heat the substrate during deposition for practical reasons such as presence of photo-resist used for lift-off, or simply because it is not possible in the equipment. In this case, it is still interesting to enhance the properties of the samples by a post-deposition annealing.

As it was already discussed in section 5.3.1, an annealing has a similar effect as a deposition on a heated substrate. However, during deposition the temperature has a larger effect because the atoms are not immediately oxidized and are on a free surface. In post-deposition annealing, the atoms are already mostly oxidized and are embedded in a 3-D lattice, which results in a much lower mobility. To obtain the same effect with a post-deposition annealing as with a substrate heated during deposition it is therefore necessary to have a much larger temperature. This process of post deposition annealing is described with more details in this section.

Two types of annealings were done here. First in a rapid thermal annealing (RTA), under argon atmosphere. The samples were annealed at 100°C for 15 min, then cooled down and analyzed (Hall measurement and optical transmission), then annealed for 15 min at 200°, etc. up to 700°C. It is important to note that, in this section, the samples that are designated as "annealed at 400°C" are therefore annealed at 100, then 200, then 300 and finally 400°C, which will not be the case in Chapter 6. The chamber of the RTA was purged with argon for 10 min, then the heating was done in 30 s, the temperature kept for 15 min, and finally the cooling was done naturally. The argon used contains maximum 1 ppm of water and oxygen but residual oxygen can remain in the chamber. These annealings have been done on the samples deposited at various oxygen concentrations. The 15 minutes of annealing have been chosen arbitrarily for practical reasons and do not allow to have an estimation of the kinetic of the annealing.

Therefore, a second type of annealing was done in a chamber under

nitrogen, with continuous measurement of the resistance of the sample. This way, it was possible to see in-situ the evolution of the properties with time and temperature.

5.4.1 Electronic properties

Hall measurements have been carried out on the samples deposited at various oxygen concentrations and annealed at different temperatures, up to 700° C and the results are depicted in Fig. 5.15. The results for the samples deposited at 17.5 and 22.5% oxygen have not been represented for clarity reasons.

The electronic density increases for all samples when an annealing is performed, up to 300°C. The absolute increase is always similar ($\sim 10^{20}$ cm⁻³), resulting in a large relative augmentation for the sample with the lowest initial density (×47), and a lower increase for the sample with the highest initial concentration (×1.1). This increase of the charge carrier density is associated with Al dopants that would be thermally activated.

The samples deposited with higher oxygen concentration have Al atoms that form Al_2O_3 that can not participate to the conduction and can not be thermally activated. One could then assume that the absolute increase of the charge carrier density would be more important for the samples deposited with lower oxygen concentration. However, these samples contain Zn metallic clusters and interstitial Zn that increase the electronic density. When they are annealed, more Al dopants are activated (*n* increased), but Zn atoms are also oxidized, reducing the electronic density. These two effects seem to compensate each other so that the absolute increase of the electronic density is almost constant, whatever the oxygen concentration used during deposition.

The electronic mobility also increases with an annealing at low temperature ($< 300-400^{\circ}$ C). The largest relative increase of mobility is observed for the samples deposited at 10 and 35% oxygen, where the mobility was increased of a factor 5.4 and 3.8 respectively. This is because there are two possible origins for the increase of mobility.

First, the annealing reduces the defects present in the films. The samples



Figure 5.15: Charge carrier mobility (Top) and density (Middle), and resistivity (Bottom) of AZO samples deposited at various oxygen concentrations and annealed at various temperatures. The error bars represent the standard deviation of the measurements.

that are almost stoichiometric are however quite stable at such low temperatures because of their high melting point. The sample deposited with only 10% oxygen is therefore the most sensitive to the annealing that oxidizes the metallic defects, due to the residual oxygen in the RTA.

The second origin to an increased mobility can be the screening of the defects in the crystal. The higher the electronic density, the better the screening of the static defects that diffuse the charge carriers, hence a better mobility. The increase of mobility due to this effect is therefore the most important in the sample deposited at 35% oxygen, because of its highest relative increase of electronic density. Note that even if the sample deposited at 35% oxygen has the highest relative increase of mobility, it remains the sample with the lowest mobility due to the alumina clusters that are present, and the low electronic density. The sample deposited at 20% oxygen is the optimal situation, where there is not much metallic atoms nor alumina clusters, and a high electronic density to screen the static defects, resulting in the sample with the highest electronic density and mobility, and lowest resistivity.

When the annealing is done at a temperature higher than 300° C, a drop in the electronic density and mobility is visible, except for the samples deposited in the beginning of the transition regime (10-15%). The drop in the carrier density must be due to an inactivation of the aluminum dopants, maybe trough formation of Al₂O₃ due to the residual oxygen present in the annealing chamber.

For the samples deposited at 10 and 15% oxygen, this drop is visible only at higher temperatures. This is probably just a kinetic effect because these samples contain metallic clusters and probably lots of point defects such as Zn_i as well. Therefore, more oxygen needs to react with the samples to transform the Zn and Al atoms in ZnO and Al₂O₃. Because of the low amount of oxygen present in the chamber, 15 min is not enough to reach the equilibrium and several additional annealings are necessary for these samples to obtain the same result as for the other samples. After the transition all the samples tend to the same constant charge carrier density (~ $2 \cdot 10^{19}$ cm⁻³).

After this transition temperature, the mobility drops because there are

aluminum atoms that act as scattering centers in Al_2O_3 , and the decreased carrier density does not allow a good screening of the defects. The drop in mobility, as for the density, is less steep for the samples that initially have metallic clusters but they eventually tend to the same mobility as the other samples.

The mobility is however not constant with the annealing temperature, after the drop due to the formation of alumina clusters. A slight increase is observed as the annealing temperatures increases, possibly due to the disappearance of defects such as dislocations, and due to grain growth as observed in Fig. 5.4. The result is a resistivity that first decreases with temperature up to 300° C due to the activation of dopants. Then it increases abruptly due to the creation of Al₂O₃ (resistivity multiplied by a factor ~ 250 for the samples in the transition regime). Finally the resistivity decreases again slightly because of the decrease of the defect density accompanied with an increase of mobility.

To confirm that the increase of resistivity is due to residual oxygen, and to analyze the kinetics of the annealing, 4 probes measurements have been done on a sample from the series LOC AZO deposited with 23% oxygen, as a function of time and temperature. Unfortunately, it was not possible to combine it with Hall measurements so only the resistivity is measured. The chamber used here is assumed to be better sealed than the RTA and was purged for 10 min before starting the experiment, and kept at 1.1 bar of nitrogen to avoid the introduction of external air in the chamber. The nitrogen used comes from evaporation of liquid nitrogen so it is assumed to be pure, however some residual oxygen is always present. The results are shown in Fig. 5.16.

First, a decrease of the resistance of 60% is observed up to 300° C, stronger than what was observed in the RTA (~30%). However, the larger reduction of the resistance here is due to the longer annealing (45 min at 300° C) since we can see that the 15 min in the RTA were not enough to reach the minimum resistance. After heating to 300° C, the sample was cooled down and the resistance was almost constant. This is a characteristic of metals, where the electronic density is considered as constant with temperature. The almost constant resistance with temperature also indicates that the electronic mobility is controlled



Figure 5.16: Resistance measured in van der Pauw geometry, of a sample of AZO deposited with 23% oxygen, as a function of time, during an annealing under nitrogen.

by defects more than by phonons.

After the cool down, the sample was heated again by steps of 50° C. Up to 300° C, no significant variation of resistance was observed. When the sample was annealed at 350° C, the resistance decreased of an additional 13%, meaning that activation of dopants is still possible, while their oxidation is not significant. At 400°C and higher temperatures, the trends reverses and the resistance increases with temperature, presumably due to Al₂O₃ formation. Note that this increase of resistance is however much slower than in the RTA since it was here kept at temperatures of 400°C or higher for 100 min and the ratio between maximum and minimum resistance is around 7, while it was around 250 in the RTA after only 15 min. This proves the need for an extremely accurate control of the atmosphere to have a good control over the properties of annealed AZO.

Finally, it can be observed during the cooling down that the resistance increases of 50% between 500° C and room temperature. This is typical

of a semi-conductor behavior where the carrier density increases with temperature. This proves that after annealing, the previously degenerate AZO becomes a semi-conductor with a Fermi level close or under its minimum of conduction band as it will be confirmed by optical measurements in section 5.4.2.

5.4.2 Optical properties

Most of the optical properties can be deduced from the electronic properties and confirm the conclusions already drawn in section 5.4.1. For clarity reasons, the results of only three samples are shown in Fig. 5.17 (beginning (15%) and middle (20%) of the transition regime, and beginning (30%) of the oxidized regime). Based on the transmission spectra, the optical bandgap has been studied and is shown in Fig 5.18. Note that, as already discussed, the sample deposited with only 10% of oxygen contains lots of Zn metallic clusters that give a partially metallic behavior to the sample and gives an aberrant value for the extracted optical bandgap. It is however plotted in the figure to show the evolution with the annealing temperature.

The sample deposited in the oxidized regime (30%) is already well oxidized as deposited, meaning that the transmission in the visible range is good without annealing. With annealings up to 300° C, the carrier density is slightly increased so the optical bandgap increases a bit due to the Burstein-Moss effect and the transparency increases in the near-UV range. After an annealing at higher temperatures (>400°C), the carrier concentration drops and the optical bandgap drops again to the value of iZnO (~3.3 eV), meaning that the Fermi level is indeed close to the minimum of conduction band.

The sample deposited in the middle of the transition regime (20%) is almost stoichiometric but contains lots of defects such as interstitial Zn that absorb visible light. An annealing at low temperature ($\leq 300^{\circ}$ C) oxidizes these defects so the optical transmission increases in the visible range. The relative increase of charge carrier due to thermal activation is low, so the optical bandgap is stable and the increased transmission in the near-UV range is due to the decreased concentration of absorbing



Figure 5.17: Transmission spectra of samples deposited with 30, 20 and 15% oxygen, as deposited and after successive annealings at different temperatures.



Figure 5.18: Optical bandgap of samples deposited at various oxygen concentration and annealed at different temperatures. The sample deposited with 10% oxygen has a metallic behavior for annealing temperatures below 500° C, giving aberrant values.

defects. Due to the high carrier density, there is absorption in the IR range. After an annealing at 400°C, the carrier concentration drops so the optical bandgap tends to 3.3 eV, and the absorption of IR due to free carrier is not present anymore.

The sample deposited in the beginning of the transition regime (15%) has a behavior similar to the one deposited with 20% oxygen. The difference comes from the metallic clusters that are present and absorb light in the whole range. Because of the high carrier density, the optical bandgap is stable up to 300°C. As shown previously, the 15 min in the RTA were not enough to reach thermodynamic equilibrium. Since the metallic clusters and interstitial zinc are present in high concentration in this sample, even after the annealing at 400°C the oxidation was not completed yet because of the low amount of available oxygen. At 600°C, the oxidation is eventually completed, the charge carrier density drops and the optical bandgap tends to 3.3 eV, and the absorption in the IR range disappears too.

It can also be seen in Fig. 5.18 that even for the sample deposited with only 10% oxygen, a semi-conductor behavior is eventually obtained and that its electrical and optical properties are similar to other samples after an annealing at $\geq 600^{\circ}$ C.

5.4.3 Nano-indentation

Lab-on-chip have been produced to test the properties of AZO thin films deposited with 13, 18, 23 and 28% oxygen ($LOC \ AZO$ series), at room temperature (see Chap. 6). Annealings have been performed on different parts of the samples at 300, 400, 500 and 700°C, for 15 min under argon atmosphere. Note that in this case, a different part of the sample has been used for every annealing temperature, instead of doing every annealing on the same part successively, like previously in this chapter. As it was already stated, an annealing of 15 min is not enough to reach the thermodynamic equilibrium. It means that we can expect that for a sample annealed 15 min at 400°C (in this section), the effect of the annealing is less visible than for a sample annealed successively at 100, 200, 300 and finally 400°C.

For the electric properties of the $LOC \ AZO$ series, a transition is observed similarly to what was observed in section 5.4.1. However this transition is here observed between 400 and 500°C instead of between 300 and 400°C due to the kinetics of the annealing. The results are presented in Fig. A.2. The transition for the sample deposited with the less oxygen (13%) is also observed at a higher temperature due to the large amount of Zn that needs to be oxidized. The mobility and density of the charge carriers could not be measured accurately due to the degradation of the Al contacts at 700°C.

The evolution of the Young's modulus and hardness extracted by nanoindentation shows no large variation with the annealing temperature. A slight decrease seems however to be present when the temperature is increased, which is coherent with what was observed in Ref. [154]. Superimposed to this slight decrease, a small step seems present around the transition temperature. This could be another indication of the formation of alumina clusters at this transition temperature, since dense



Figure 5.19: Young's modulus and hardness as a function of the annealing temperature (15 min under argon atmosphere), for AZO thin films deposited at different oxygen concentrations.

amorphous alumina thin films deposited by reactive sputtering have shown a higher Young's modulus (179 GPa) and hardness (12 GPa) than what is observed here for AZO.

When the oxygen concentration is increased from 13 to 18%, the Young's modulus and the hardness decrease from 123 ± 11 to 111 ± 9 GPa and from 9.8 ± 1.2 to 7.4 ± 0.9 GPa, respectively. This could be explained by the apparition of the amorphous, less dense, grain boundaries due to the lower mobility of atoms during sputtering, as already discussed in section 5.3.1

5.5 Conclusions

Reactive sputtering is a technique that allows a large variation of the stoichiometry in oxide thin films. The level of oxidation is crucial for the properties of AZO since a common application is transparent electrodes, and a film that is not completely oxidized is not well transparent and does not have the highest possible conductivity. On the other hand, if too much oxygen is incorporated in AZO, the conductivity can drop by nearly four orders of magnitude. Another important parameter is the temperature, during deposition or in a post-deposition annealing. This has also been studied as a way to improve the properties of the thin films.

In MEMS and flexible electronics, if too high stresses are present in a thin film it can lead to dramatic consequences and must therefore be avoided. In this chapter, we monitored the stress during deposition thanks to the MOSS technique, along with other classic characterization techniques for the structural (SEM, XRD), chemical (ICP-OES), optical (photospectrometry), electrical (Hall measurements, piezoresistance), and mechanical (nano-indentation) properties.

Thanks to these multiple characterization techniques, it was possible to prove that intrinsic defects of ZnO are detrimental to the optical and electrical properties of AZO since they limit the mobility and only slightly contribute to the charge carrier density. Enough oxygen must therefore be introduced to limit the oxygen vacancy and interstitial zinc. Too much oxygen is even more detrimental since it favors the apparition of alumina clusters that decrease the charge carrier density and mobility.

Increasing the temperature, during or after deposition, has been proven as an efficient way to highly increase the transparency and the conductivity. If possible, heating during deposition instead of an annealing is preferable since it leads to a lower resistivity, higher transparency and a lower tensile stress, while requiring a lower temperature (180 instead of 300° C). The increased temperature enhances the properties through different mechanisms such as a decrease of the intrinsic defects, by favoring the oxidation of zinc atoms, and activating the Al dopants so that they contribute to the conduction. Like for the oxygen, an optimum is found because a too high temperature favors the apparition of alumina clusters, even if the annealing is performed under an inert gas such as argon.

Figure 5.20 shows the evolution of the maximum of transmittance T_{max} (for the transmission peak around 650 nm) and the sheet resistance R_s for different oxygen concentrations and annealing temperatures, for different deposition temperatures, and for the ZnO thin films discussed in Chapter 4. The curves of constant figure of merit (defined by equation 1.3 assuming that $R \simeq 0$) are also indicated to compare the quality of the different layers. This confirms that iZnO is indeed not adapted for transparent electrodes, and that the middle of the transition regime (around 20% oxygen here) gives the optimal properties. It also confirms that heating during deposition around 180°C gives the best results but an annealing at 300°C after deposition tends to give similar results.



Figure 5.20: Evolution of R_s and T_{max} for different series of samples. The arrows indicate the direction of increasing annealing temperature for the series AZO O, of increasing deposition temperature for the series AZO T, and of increasing oxygen concentration for the series of ZnO samples. The dotted lines represent the curves of constant figure of merit (defined by equation 1.3 assuming that $R \simeq 0$).
Chapter 6

Electromechanical characterization of thin films

The effect of stress can be of primal importance in thin films, especially in MEMS or flexible electronics. Internal stress often appears during deposition steps and can be analyzed with a technique such as the MOSS. However, this tool can only characterize the stress, not its effect on other properties. Indeed, in order to change the stress in a material the deposition conditions must be changed. This often implies a variation in the micro-structure or the stoichiometry, meaning that it is difficult to study the impact of the stress only. To extract the impact of a stress on the properties of a thin film it is therefore more interesting to apply a deformation after the deposition. One possible way is by deforming the substrate. The problem is that polymer substrates often lead to different properties and make annealing or high temperature deposition impossible, and silicon substrates limit the applied deformation to about 0.1% before fracture. For this reason, it is more interesting to apply a loading on a free-standing thin film after deposition.

For this purpose, the lab-on-chip technique has been developed at UCL in 2008, where a second material with internal stress is used to pull on the studied thin film. [155] The first thesis using this thesis was presented in 2012, [156] where the theoretical bases have been set, the geometrical

optimization and the errors have been analyzed. That generation of labon-chip focused on the mechanical testing only. Later, piezoresistance of silicon has been studied using the same principle. [157]

In this thesis, new structures have been added and other have been optimized according to the experience acquired over the years, especially for brittle materials with a low fracture strain. Only the basic theory will be reminded here, for a complete theoretical analysis, refer to Ref. [156]. The focus in this chapter will be on the new structures and the fabrication process, illustrated with some results obtained for ZnO thin films.

6.1 Basic principle

The technique is used to extract the stress-strain curve of thin films, from the elastic regime up to the fracture strain. It was initially designed for metals with high fracture strain so it had to apply large deformations. Here the focus was on brittle materials, hence on the elastic regime $(\varepsilon < 1\%)$.

To avoid using an external (electro-)mechanical actuation to apply the force on the sample, a second material with tensile internal stress is used to fabricate "micro-springs" (actuators) attached to the sample (specimen) layer. During the fabrication process, both the sample and the actuator can not move due to the adhesion to the substrate. When they are released from the substrate, the actuator pulls on the sample until the force equilibrium is reached. The principle of the fabrication process is shown in Fig. 6.1, and the principle of the determination of the stressstrain curve is shown in Fig. 6.2. If the mechanical properties of the actuator are well known, measuring its displacement gives the applied force. If the thickness of the specimen is known, one elementary structure (called "micro-machine") gives one point of the stress-strain curve of the material. The position of this known point on the stress-strain and the actuator.



Figure 6.1: Principle of the fabrication process of an elementary structure of the lab-on-chip technique.



Figure 6.2: Principle of the determination of the force-displacement (stress-strain) curve of the sample material up to fracture, using several micro-machines of different dimensions.

One of the greatest advantages of micro-fabrication technology is the possibility to easily produce thousands of structures on a single wafer. Therefore, masks have been designed with a large number of these elementary structures with different dimensions so that points of the whole stress-strain curve can be obtained. Structures with different dimensions are used to obtain the stress-strain curve, but every dimension can be reproduced several times to make a statistical analysis of the material properties.

It is important to note that the lab-on-chip technique does not give the stress-strain curve of a specimen, contrary to other techniques such as the push-to-pull. Instead, it gives a set of stress-strain points taken on different specimens. This means that the sample and actuator layers must be homogeneous on the sample to obtain meaningful stress-strain curves.

6.1.1 Pros and cons of the lab-on-chip technique

A brief summary of pros and cons is presented here. For a complete comparison with other mechanical testing of thin films, see Ref. [156].

Advantages:

- Easy fabrication process. Compared to other techniques used to extract stress-strain curves, this technique only uses 2, or maximum 3 different layers, with no deep etching that can be difficult to master.
- On-chip loading. No external equipment is needed to apply the force on the sample meaning that the load can be applied for months or even years, so that stress relaxation can be studied over large periods of time. The on-chip loading also implies compact samples that can be fitted in/under other equipments such as Raman spectroscopy, photo/cathodo-luminescence, or in a magnetic field for Hall measurements.
- **Statistical analysis** is possible due to the very large number of samples fabricated at once.

• No "machining" of the specimens. The specimens are here patterned by lithography so that no focused ion beam (FIB) step is required, which can induce defects and/or contamination in the studied specimen.

Drawbacks:

- The release requires to find a sacrificial layer that can be etched without etching the sample nor the actuator. This remains the main problem for a routine application on different materials, even though the XeF₂ release discussed later could be the way to solve this problem.
- The homogeneity needed in the layers is crucial. Indeed, the mismatch of the actuator material is measured in a different place than where the tensile testing is done. If the actuators are not homogeneous over the whole substrate (intrinsic properties, or geometry due to the lithography), large errors can appear in the extracted stress-strain curves.
- On-chip loading. Even though it is one of the main advantages of the technique, it is a problem if the stress-strain curve changes quickly. The loading starts as soon as the release of the actuators begins, and the measurement of the stress-strain curve usually begins more than one hour later. It is therefore impossible to access to the mechanical response during the first hour. It was for example a problem for pure aluminum thin films, where the stress relaxation was really quick (see Ref. [156]). Again, XeF₂ release could be a significant advancement to reduce this minimum time before measurement.

6.1.2 Data reduction of an ideal structure

The following notations will be used throughout this chapter:

ε^{mis}	Mismatch strain due to the deposition of a layer
σ, ε and ε^{mech}	True stress, total and mechanical strains, respectively
E and ν	Young's modulus and Poisson ratio
L_0 and L_0^{free}	Length of beams before release, for a constrained and free beam, respectively
u and u^{free}	Displacement after the release, as defined in Fig. 6.2. Defined as positive when the actuator pulls on the sample.
S and S_0	Cross-sectional area of a beam, after and before release, respectively

The subscripts $_a$, $_s$ and $_{sub}$ refer to the actuator, the specimen and the substrate respectively.

The actuators are considered as linear elastic springs so, if their mechanical behavior is well known, the measurement of u gives the force applied by the actuator on the sample. The force applied by the actuator is proportional to the mechanical strain:

$$\varepsilon_a^{mech} = \varepsilon_a - \varepsilon_a^{mis}$$
$$= \ln\left(\frac{L_{a,0} - u}{L_{a,0}}\right) - \varepsilon_a^{mis}$$
(6.1)

$$\simeq -\frac{u}{L_{a,0}} - \varepsilon_a^{mis} \tag{6.2}$$

The linear approximation is justified because the strain in the actuator is small (<0.4%). The force applied by the actuator is therefore given by:

$$F = E_a S_a \varepsilon_a^{mech}$$
$$= E_a S_a \left(-\frac{u}{L_{a,0}} - \varepsilon_a^{mis} \right)$$
(6.3)

Note that due to the convention sign chosen for u, ε_a^{mis} is defined as negative when the actuator is deposited with tensile stress, which is always the case.

The mismatch can be calculated by several methods. The first one was the measurement of the displacement of an actuator free beam, meaning that $\varepsilon_a^{mech} = 0$, leading to:

$$\varepsilon_a^{mis} = \ln\left(\frac{L_{a,0}^{free} - u^{free}}{L_{a,0}^{free}}\right) \simeq -\frac{u^{free}}{L_{a,0}^{free}}$$
(6.4)

This technique however is not accurate because a free beam almost always goes out of plane due to stress gradients, leading to errors during the displacement measurement. To ensure that the beam stays in the same plane as the reference cursors, self-actuated structures have been developed. In these structures, the "specimen" beams are actually made of the same material as the actuator, but have different dimensions than the actuators. This leads to an actuator mismatch given by:

$$\varepsilon_a^{mis} = \frac{w_s \frac{u}{L_{s,0}} + w_a \frac{u}{L_{a,0}}}{w_s - w_a} \tag{6.5}$$

The stress in the sample is calculated directly from the force applied by the actuator, divided by the section of the sample:

$$\sigma = \frac{F}{S_s} = E_a \frac{S_a}{S_s} \left(-\frac{u}{L_{a,0}} - \varepsilon_a^{mis} \right)$$
(6.6)

The strain in the sample is calculated from the displacement u. Here, the small deformation approximation is not always true, meaning that we must consider the following expression of the strain:

$$\varepsilon_s = \varepsilon_s^{mech} + \varepsilon_s^{mis} = \ln\left(\frac{L_{s,0} + u}{L_{s,0}}\right)$$
(6.7)

To obtain the mismatch of a thin film, a technique that is also widely used is Stoney. For the actuator material, the self-actuated micromachines give a more accurate result because there is no need to know the Young's modulus, nor the Poisson ratio. If the sample has tensile stress, these structures can also be used for the sample material. If the sample contains compressive stress however, this technique becomes unusable because buckling makes the structures go out of plane. In this situation, Stoney is the best way to evaluate the mismatch. As shown in section 3.3, the stress can be evaluated as:

$$\sigma_s = \frac{1}{6} \frac{E_{sub}}{1 - \nu_{sub}} \frac{h_{sub}^2}{h_f} \Delta \kappa \tag{6.8}$$

The mismatch of the thin film (actuator or sample) is then given by:

$$\varepsilon_s^{mis} = \sigma_s \frac{1 - \nu_s}{E_s} \tag{6.9}$$

The problem is that the Young's modulus and Poisson ratio are often not well known, since it is the goal of the lab-on-chip. However, if the mismatch strain is calculated with the self-actuated micro-machines and the Young's modulus can be well characterized by another technique, this is a way to calculate the Poisson ratio of the thin film.

Another relation that is important to design the dimensions of lab-onchip is the expected displacement of the cursors for a model material. Indeed, the cursors need to move of a measurable distance or the error on the measurement of the displacement will be large. For a linear elastic sample the expected displacement is given by:

$$u = \frac{E_s S_s \varepsilon_s^{mis} - E_a S_a \varepsilon_a^{mis}}{\frac{E_s S_s}{L_s} + \frac{E_a S_a}{L_a}}$$
(6.10)

where ε^{mis} is defined as negative for tensile strain.

6.2 Different fabrication processes

Since this thesis mainly focused on the development and extension of the lab-on-chip technique, the history of the evolution of the different possible fabrication processes will be described with their advantages and drawbacks. The difficult step in the fabrication process is the release of the micro-machines, and dictates what type of process must be chosen. This thesis was focused on brittle materials (oxides) but other materials were tested as well, and their process fabrication will be presented too.

6.2.1 Actuator selection

First it is important to identify the material that will be used as actuator since it is the first layer that is deposited, and the whole lab-on-chip technique relies on the good knowledge of the actuators. The perfect actuator must have several properties:

- Linear elastic behavior when unloaded for an easy extraction of the applied force. If there is plasticity in the actuator, the force can not be only calculated with the measurement of u.
- Brittle fracture. One could expect the actuator to have a decreasing stress during the release step (see Fig. 6.2), however, it can locally increase at some points due to stress concentrations. If the stress increases too much, it is better to have a brittle fracture than plasticity. Indeed, if plasticity occurs the calculation of the applied force would be erroneous and no visible sign would warn the user about the error.
- No stress relaxation. To characterize the stress relaxation of a sample, the actuator must be absolutely stable in time.
- **High mismatch strain.** To obtain a large displacement that can be measured accurately, a high mismatch is important.
- Large Young's modulus. For a fixed mismatch, a larger Young's modulus will create a lager displacement. In addition, a larger Young's modulus allows to decrease the thickness of the actuator, limiting the problem of fracture at the overlap.
- Thermal and chemical stability. During the process the actuator properties must not change, especially during the release step, where the substrate (sacrificial layer) must be etched, without etching the actuator. Thermal stability is important if the sample is deposited or annealed at high temperature.
- Homogeneous and reproducible deposition is necessary for the lab-on-chip technique to work. Indeed, it is based on the as-

sumption that every actuator and sample beam have the same mechanical properties.

The material that has been selected for these reasons is LPCVD (low pressure chemical vapor deposition) silicon nitride (Si_3N_4) that meets all these requirements. The only drawback is that LPCVD Si_3N_4 is deposited at high temperature $(800^{\circ}C)$, practically limiting the substrates to bare silicon, or silicon with SiO₂ used as a future sacrificial layer. If an other sacrificial layer is used, LPCVD Si_3N_4 must be replaced by PECVD (plasma enhanced chemical vapor deposition) Si_3N_4 deposited at 300°C. However, the latter has a lower mismatch, poorer chemical stability (unless it is annealed) and a lower homogeneity (between 5 and 10% difference of thickness between two opposite sides of a substrate). LPCVD or PECVD silicon nitride will therefore be preferred in a process depending on the used sacrificial layer, as it will be detailed in the next sections that present the different available fabrication processes.

6.2.2 SiO₂ sacrificial layer and HF release

At the beginning of the lab-on-chip technique, a sacrificial layer was deposited before the actuator (between step (a) and (b) in Fig. 6.1). The goal of this layer was to be etched away as fast as possible, without etching the sample nor the actuator. Typically the sacrificial layer had a thickness around 1 μ m. A thick sacrificial layer implies longer deposition time, an increased roughness and possibly a poorer anchorage if the sacrificial layer is soft compared to the tested layers. A thin sacrificial layer increases the risk of stiction. A thickness around 1 μ m seems to be a good compromise.

The sacrificial layer chosen for metal lab-on-chip was SiO_2 because of its fast etching in HF compared to metals (high selectivity). PECVD SiO_2 was chosen because it is etched around one order of magnitude faster than thermal SiO_2 , leading to a shorter release in HF, hence less damage on the sample and actuator layers. LPCVD Si_3N_4 , despite its good chemical stability, has an etching rate around 9 nm/min in the HF 73% used for the releases. The release time can be tuned depending on the properties of the PECVD parameters leading to different oxide quality. A typical release is around 1 min, not too long to limit the etching of other layers, not too short to be controllable. This leads to an average etching of the actuators of about $1.5 \times 1 \text{ min} \times 9 \text{ nm/min} = 13.5 \text{ nm}$. The 1.5 factor comes from the fact that the actuators are etched from the top, and from the bottom on the released parts.

The HF release is a wet etching, meaning that a critical point dryer (CPD) is required to avoid stiction of the structures. This means that after the end of the release, the sample must be rinsed in several baths of isopropanol (IPA) before being introduced in the CPD. The IPA is then replaced by liquid CO_2 , the pressure and temperature are increased to obtain supercritical CO_2 . The pressure is then decreased down to atmospheric pressure and the sample is cooled down to evaporate the CO_2 . The goal of this process is to avoid interfaces between liquid and gaseous phases so that no capillarity forces are present, and stiction can be avoided. This step however induces some stress on the samples when the IPA is replaced by liquid CO_2 (turbulence that can damage the sample if the films are only a few nm thick), and takes around one hour (problem for thin films with a quick stress relaxation).

This process could not be used for ZnO thin films because an etching rate higher than 150 nm/min was measured in HF.

6.2.3 Polymer sacrificial layer and O₂ plasma release

Silicon oxide can be used as a sacrificial layer for metals because its nature leads to a high selectivity during HF releases. However if the sample is an oxide too, it is very likely that it will be etched in HF, leading to a poor selectivity and an impossibility to use the lab-on-chip technique.

To obtain an infinite selectivity, a polymer layer (PolyImide) was used as a sacrificial layer. For this process, the polyimide (PI) is spin-coated with a thickness around 1 μ m and annealed at 350 °C to ensure a good thermal stability. Then PECVD Si₃N₄ is deposited at 300 °C and patterned with plasma etching. The sample is then deposited on photoresist patterned by lift-off. Finally, the release is done by etching the sacrificial layer in an oxygen plasma that does not etch the actuators nor metal oxides at all. This infinite selectivity is the big advantage of this process. Another great advantage is that the release is done by dry etching, meaning that no CPD is needed and the samples can be observed around one hour earlier than with the HF process. However, this process also induces several problems:

- PECVD Si_3N_4 must be used to have actuators deposited at a temperature that does not burn the PI.
- The roughness of the PI leads to a roughness of the actuators and sample layer. This roughness also diffracts the lasers of the MOSS, making stress measurement impossible. It also makes ellipsometry inaccurate, which is a problem to determine the thickness of the actuators and samples.
- Polyimide has a low Young's modulus (~ 2.5 GPa) compared to the thin films on top of it, offering a poor mechanical anchorage. This could be the origin of the nonsensical results obtained for ZnO thin films with this process (see Fig. 6.7). This process however gave interesting results on alumina thin films [158] so the problems with ZnO thin films might have a more complex origin.

6.2.4 Si substrate as sacrificial layer and TMAH release

For oxide samples, it is very unlikely to have a good selectivity when the sacrificial layer is also an oxide and the release is done with acidic solutions. Therefore, a possibility is to use the silicon substrate as a sacrificial layer. The advantages of this process are:

- No sacrificial layer means one fabrication step less.
- The actuators and samples are deposited on an extremely flat surface, compared to the PECVD SiO₂ and PI.

• The actuators and samples are deposited directly on silicon, which is the ideal situation for the ellipsometric characterization needed to have a accurate measurement of the thickness of the different layers.

Wet etching solutions of silicon can be grouped in two main categories:

- Isotropic etchants are usually composed of a strong oxidizer to form a SiO_2 layer at the surface of the silicon, and an acid such as HF to etch the SiO_2 . A typical solution is HNA, composed of Hydrofluoric, Nitric, and Acetic acids. This is however not compatible with most oxides and metals.
- Anisotropic etchants are usually hydroxides such as KOH or TMAH (Tetra Methyl Ammonium Hydroxide). Many oxides and metals are not etched by hydroxides so this option was chosen.

Since a good selectivity is mandatory, anisotropic etching of the silicon substrate was chosen. However, this implies that the beams must be tilted of 45° compared to the cleavage directions of the silicon substrates. To cut the samples, dicing is therefore mandatory, as well as a coating of protective resist.

It is often considered that a selectivity higher than 1000 is necessary for lab-on-chip, meaning that to release the 14 μ m wide actuators, a maximum of ~ 7 × 1.5 = 10.5 nm are etched in the sample layer. Note that in wet etching, the inter-granular etching is often faster than the intra-granular etching. Therefore, even with a selectivity of 1000, a film thicker than 100 nm could be completely broken up because all the grains are separated from each other through dissolution of the grain boundaries.

The difficulty with ZnO thin films is that they have an amphoteric behavior, meaning that they are etched in both acidic and basic solutions: [159]

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$$
$$ZnO + H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$$

The etching rate of silicon in TMAH varies over more than two orders of magnitude depending on the concentration and temperature. When the concentration is increased between 0 and 5% the etching rate increases, then saturates and decreases slightly when the concentration is increased because the etching requires both OH^- and H_2O . A better homogeneity of etching is obtained as the concentration is increased, and the etching rate increases exponentially with temperature. For these reasons, the etching of silicon with TMAH is usually done around 80°C with a concentration of TMAH between 10 and 25%. Etching rates from the literature for silicon at different temperatures and concentrations are shown in Fig. 6.3, along with etching rates measured on ZnO in this work.

It can be observed that the etching rate of ZnO also increases with temperature. The etching rate increases with TMAH concentration much faster for ZnO than for silicon, meaning that the best selectivity is obtained at lower concentrations. These concentrations however lead to a highly heterogeneous etching, meaning that some points are released before others and a longer etching must be done to be sure that all points are released. After optimization of the etching parameters, the maximum selectivity was still under 100, meaning that this process is not adapted to ZnO thin films.

This process was however adapted successfully for metallic glasses (ZrNi [160]). It also showed a good selectivity for nickel thin films and several oxides such as ZrO_2 and SiO_2 .

6.2.5 Si substrate as sacrificial layer and XeF₂ release

As previously said, a dry release of the structures presents several interests but a polymer sacrificial layer is not suitable for mechanical testing. Dry etching of the silicon substrate (used as sacrificial layer) has therefore been investigated. Two options were considered. First, SF₆ plasma etching was studied during Dr. Coulombier thesis [156]. The difficulty is that the Si₃N₄ actuators are also etched by the types of plasma that etch silicon, meaning that the actuators need to be protected during release and the protection needs to be removed afterwards.



Figure 6.3: (Top) Etching rate measured for ZnO thin films in a 2% TMAH solution, as a function of temperature. (Bottom) Etching rate of silicon in TMAH for different temperatures and concentrations, taken from Ref. [161] (solid lines), compared to the etching rate of ZnO thin films for different TMAH concentrations obtained in this work (dashed line).

The second possibility, that has been studied in this thesis, is the etching of silicon in XeF_2 . Note that XeF_2 is a gas and not a plasma contrary to the SF_6 etching, meaning that it can be done in a simple Plexiglas chamber, where an optical microscope can be fitted, allowing to observe the release in real-time. This is very interesting because, to be sure that everything is released, an over-etching must be done with other processes. This over-etch can lead to large errors in the estimation of the stress and etches unnecessarily the samples and actuators if the selectivity is not infinite. The XeF_2 etching is isotropic, quick, and has an infinite selectivity with a large number of materials (we tested Pt, Pd, Al, Ni, Cr, ZrNi, ZnO, AZO, Al₂O₃, ZrO₂). Graphene is not etched by XeF_2 but is fluorinated. In general, oxides are almost not etched by XeF_2 except for VO_2 where a relatively fast etching was observed during this thesis (selectivity inferior to 1:100). SiO₂ has a very high selectivity with Si (1:1000-10 000 typically), meaning that Si parts that must not be etched can easily be protected with a small oxidation. This also means that the native oxide can be problematic during the release of MEMS if it is not removed.

The main problem with XeF_2 is the selectivity with the Si_3N_4 that is commonly used as actuator (see section 3.7 for more details).

6.3 Detailed process with XeF₂ release

Here is the detailed fabrication process used for the samples that gave the best results for ZnO thin films.

Substrates cleaning

The substrates used have a diameter of 3 inches, a thickness around 380 μ m, an orientation $\langle 100 \rangle$ and are polished on one face. They are cleaned in a succession of bathes:

• Piranha acid: H₂SO₄+H₂O₂ (5:2) at 120°, 10 min, to remove the organic contamination and oxidize the surface.

- Rinsed in deionized (DI) water for 10 min.
- HF (2%) dip for 15 sec to remove the oxide layer.
- Rinsed in DI water, 2×10 min in different baths
- Spin rinser dryer.

LPCVD Si₃N₄ deposition

The Si₃N₄ used for the actuator is deposited in a LPCVD furnace (VF-1000LP from Koyo) at 800°C. The precursors gas are SiH₂Cl₂ (30 sccm) and NH₃ (120 sccm) and the pressure is 0.35 mbar. Typical thicknesses are less than the half of the thickness of the specimen layer (70-150 nm for a sample of 150-300 nm).

Positive lithography

To pattern the actuators, a positive lithography is used. Before enduction, a monolayer of adhesion promoter (HMDS) is deposited on the sample in a LP-III oven, in vapor phase. The positive photoresist (AZ6612) is then spin-coated at 4000 rpm and baked at 110° C for 90 s. The resist is then exposed around 3.2 s with an intensity of 10 mJ/cm².s. The development is done for 60 s in AZ 726 MIF (diluted TMAH with a surfactant). After the development a second baking is done at 130° C for 90 s to increase the stability during plasma etching.

Actuators etching

Before this thesis the etching of the actuators was done in an SF₆ plasma. The problem is that this plasma etches silicon around 10 times faster than Si₃N₄. To be sure that the actuators are completely etched, an over-etch of about 10% of the time is a good practice, leading to a significant etching of the silicon substrate. This leads to a high step that favors fracture of the sample at the overlap during the release. To avoid this problem, the plasma has been changed to CHF₃ that has a

selectivity with silicon of about 1:3, limiting the over-etch in silicon to a few nanometers. After the CHF_3 plasma, the photo-resist is not well removed by acetone. Therefore, an oxygen plasma or a piranha cleaning is a better choice. Note that both create a layer of oxidized silicon that must be removed (HF or argon plasma) to avoid problems during the XeF₂ release.

Lift-off lithography

A layer can be pattered by two ways: deposition on the full wafer and then etching, or by lift-off after deposition on a patterned resist. Plasma etching of ZnO is difficult and wet etching results in a large roughness (>500 nm) of the edges. Lift-off has thus been chosen to pattern the sample. The negative photoresist used for the lift-off is the AZ5214E, spin-coated at 4000 rpm and baked at 110°C for 90 s. A first UV exposure of 2 s is done to define the patterns. Then a baking of 40 s at 120°C is followed by a flood exposure (fully transparent mask) of 7 s to inverse the resist. Finally the development is done in AZ 726 MIF for 90 s. The photoresist thickness is around 1.4 μ m with this process. Depending on the deposition technique it is recommended to deposit less than 500 nm (e-beam evaporation) or 300 nm (sputtering) to obtain a good lift-off. Thicker films could cover the edges of the photoresist and make the lift-off impossible. If it happens, putting the sample in ultra sound for 1 hour can help but there is a risk of damaging the sample if some layers have a poor adhesion.

The covering of the steps during sputtering has two origins. First, the mean free path of the sputtered molecules at 2 mTorr is on the order of a few cm, meaning that they experience some collisions between the target and the sample. This leads to a deposition that is slightly conformal. Second, the sputtering target is not exactly under the sample, there is an angle of around 40° . Because the sample is rotated the resulting deposition is somewhat conformal. The photoresist induces a shading effect that prevents deposition near it. The shaded distance can, in first approximation be calculated as:

$$t \cdot \tan \alpha \cdot \cos \beta \tag{6.11}$$



Figure 6.4: Correction factor

where t is the thickness of the photoresist, $\alpha \simeq 40^{\circ}$ in our sputtering equipment is the angle between the sputtering direction and the normal to the sample, and β is the angle between the edge of the photoresist and the projection of the sputtering direction on the sample. If we consider that the deposition rate is 0 within this distance and the "plane wafer deposition rate" elsewhere, the integral of the deposition rate over one rotation of the sample (β varied from 0 to 2π) gives a correction factor for the thickness.

$$f_{\rm corr} = \frac{S}{w \cdot t_{\rm film}} \tag{6.12}$$

where S is the real section of the beam, $t_{\rm film}$ is the thickness of the film without shading effects, and w is the measured width of the beam. This correction factor (see Fig. 6.4) corresponds to the ratio between the real section of the beam, reduced due the shading effect, compared to the section it would have had if no shading effect was present. Another possibility is to define an effective width of the beam:

$$w_{\rm eff} = \frac{S}{t_{\rm film}} \tag{6.13}$$

As a rule of thumb for the sputtering equipment used during this thesis, $w_{\rm eff} \simeq w - 0.5 \ \mu m$.

Sample deposition

The deposition of the sample is done by reactive sputtering an is detailed in Chapters 4 and 5. Because of the presence of photoresist, deposition can only be done at room temperature.

Lift-off lithography and contact/tape

The third layer is patterned by lift-off similarly to the sample layer. This third layer has two purposes:

- The overlap is a weak region of the lab-on-chip because there is a step creating a stress concentration. Therefore, even if the width is larger at this point than in the specimen, the fracture often occurs at the overlap. In this case, no information can be deduced from a micro-machine. To avoid that, some "tape" is added on the overlap to reinforce it and reduce the risk of failure at this point.
- The new generation of lab-on-chip includes structures to measure electric properties that need to be contacted. This third layer is therefore used as electrical contacts as well.

To limit the number of masks and the fabrication steps, the contacts and "tape" are deposited at once. The deposited material must therefore be a metal. Aluminum was chosen because it is a common material for electrical contacts and has low internal stress. High internal stress would be a problem because it would locally curve the micro-machine, making it go out of plane. A titanium adhesion layer (3-5 nm) can be deposited before to increase the adhesion. It might be mandatory if bonding is done on the contacts.

Release

The release is done with XeF_2 , at a pressure of 3 Torr, with pulses of 2 s. The XeF_2 process is more detailed in section 3.7.

6.4 Structures for opto-electro-mechanical characterization

Different significant changes have been done during this thesis compared to previous generations of lab-on-chip:

- The dimensions of the micro-machines are designed for brittle materials, so the focus is on low deformations.
- Since the corrections necessary to take into account the effect of the actuators, clamping region and dog-bone are more and more problematic, especially at low deformation, all series have the same dimensions of actuators. The sample is now symmetric, meaning that the sample end fixture has been replaced by an overlap region identical to the one on the actuator. The use of a reduced number of actuators and and clamping regions independent of the test sample allows an easier future simulation by finite elements of the force-displacement curve for the lab-on-chip. All the major corrections could therefore be simulated once and for all, and be applied for all tested layers.
- All the actuators have a tapered shape, the rectangular ones have been removed since they do not give additional information.
- The number of types of structures has been significantly reduced. Therefore, every structure is now reproduced 12 times (12 identical dies) instead of 4 times before, which allows to study the effect of several post-deposition treatments, and perform statistical analyses.
- For narrow beams, the average thickness can be significantly different than the thickness of the film due to shading effects of the photoresist. To evaluate the real section area of the samples, beams of different sections have been placed between every dies. This allows to make cross-section SEM images to evaluate the correction factor for the sample beams, and the etching of the actuators.

The general layout of the masks is presented in Fig. 6.5, along with a view of one of the dies. In addition to the number of repetitions of each structure, several types of structures are now present on each die. Rotating sensors have been removed of the masks because for very thin films, stress gradients have always been observed to be significant and the structures went out of plane, making them useless.

The several parts of the die presented in Fig. 6.5 are detailed hereafter:

- a) "Wide range" test structures. The actuators cover a wide range of dimensions to obtain the full stress-strain curve on different materials. Their width goes from 10 to 14 μm, with an average of 12 μm. There are 30 actuators per series of micro-machines, identical for every series. Four different widths (1, 1.5, 2.5, 4 μm) and lengths (50, 100, 200, 400 μm) of samples are present leading to sixteen series of micro-machines allowing to study size effects. The symmetrical specimen allows an easier data correction, and the anchorage in actuator material avoids buckling of the anchorage for samples with compressive stress. Detail in Fig. 6.6a.
- b) "Piezo-resistance" test structures. It was initially designed with two contacts for silicon, that has a large piezo-resistive coefficient. The problem is that the contact resistance varies from one micro-machine to another one and this variation is indistinguishable from the piezo-resistive effect. For samples with a smaller piezo-resistive coefficient, the design has been changed to a four contacts geometry. Samples with lengths of 50, 100, 200 and 400 μ m are present, with a width of 3 μ m for both arms of the loop. The actuator is here wider, going from 14 to 18 μ m. The contacts and samples are either free-standing after the release, or deposited on the actuator layer to avoid short-circuits. The actuator must therefore be made of an insulating material such as Si₃N₄. Detail in Fig. 6.6b.
- c) "Self-actuated" test structures have been added for the sample material too, allowing a more accurate measurement of the mismatch if the sample is deposited with tensile stress.



Figure 6.5: (Top) Full mask of the last generation of lab-on-chip. (Bottom) One of the 12 identical dies, except for the large letter (E here) that is used to differentiate the dies.

- d) "Unload" test structures. A wide beam of sample material is connected to a narrow beam of actuator material. In this case, the stress in the sample material is released and it is possible to access data of the stress-strain curve for strains lower than the mismatch strain. For a metallic sample, the unloading is also the most accurate way of measuring the Young's modulus. This type of structure however works only if the sample is deposited with tensile stress. Detail in Fig. 6.6d.
- e) "Small deformation" test structures, with large $(8 \ \mu m)$ and long (400 and 800 μm) samples, to evaluate accurately the stress-strain curve at very low deformations.
- f) "Graphene" test structures, with a large (8 μm) and short sample (20 and 40 μm) to measure large deformations (up to ~ 10%), on small samples to limit the probability of a crack. Since metallic actuators (Ni for example) seem to be the more promising way to obtain graphene lab-on-chip, it was designed assuming that the actuator is conductive. Indeed, silicon nitride has shown a poor adhesion with graphene, meaning that the actuator cannot not pull on the sample because decohesion occurs. Metallic actuators exhibit a larger adhesion with graphene, hence seems to be able to apply a force on it. In this case, two contacts probing is possible because one anchorage of the sample has been electrically isolated. The substrate is supposed to be insulating (quartz or sapphire), and the sacrificial layer (Cu) is supposed to be etched on the whole thickness to avoid short-circuits between different micro-machines. Detail in Fig. 6.6f.
- g) Large rectangle of material deposited directly on silicon for an easy measurement with ellipsometry and nano-indentation. Free beams of varying widths (from 1 to 20 μm) of sample and actuator are also present to easily visualize the underetching. Finally, marks are present to evaluate the quality of the lithography.
- h) Van der Pauw structure with four large contacts over a square of sample material deposited on the actuator material (assumed

as insulating) for electrical insulation. This allows to measure the resistivity, charge carrier density and mobility.

In addition to these structures, trial structures have been designed to measure the charge carrier density and mobility as a function of strain, and are placed outside of the dies. These structures are presented in Fig. 6.6g. Lateral contacts have been added to obtain a Hall bar, and the actuator is covered by the metallic contact. This configuration forbids the easy extraction of the stress but allows the measurement of the strain. Bonding of these structures must then be done to a PCB that can be inserted in a magnetic field to make the Hall measurement.

Finally, a large square $(2 \times 2 \text{ cm}^2)$ of the sample material directly on the substrate was added in the center of the substrate to allow the measurement of the stress profile thanks to the MOSS technique.



Figure 6.6: (a) Large range, (b) four contacts piezoresistance, (d) unload, (f) graphene, and (g) Hall micro-machine. The blue layer represents the actuator, the samples are in green and the contacts are in grey. Note that the scale is different for every structure presented.

6.5 Results

The HF process could not be used because it etches ZnO. The process on polyimide was therefore tested and stress-strain curves were obtained. An example of several curves obtained on the same ZnO sample is given in Fig. 6.7. The black line corresponds to a linear elastic behavior with a Young's modulus of 110 GPa, which is what is expected for ZnO. Every other curve corresponds to the results from a different series. One can see that there is a very large dispersion, lots of negative stress and that several curves seem to reach a plateau around 500 MPa. This behavior is attributed to the poor mechanical properties of the polyimide sacrificial layer. The maximum deformation is higher than 1% for most of the series, and even exceeds 2% in one case. These large fracture strains are not expected for ZnO thin films and are attributed to a deformation of the anchorage. Because of these results that show the limits of the polymer sacrificial layer, the other processes for oxide lab-on-chip have been developed. The process with TMAH could not give any result due to the poor selectivity with ZnO.

The process with XeF_2 gave satisfactory results for one batch of samples with ZnO thin films, where the Si_3N_4 actuators were not etched during the release. Unfortunately, the infinite selectivity with silicon nitride was probably due to a leak (or other anomaly) in the LPCVD furnace and could not be reproduced. Therefore, no viable lab-on-chip for AZO thin films could be produced. The main problem with the etching of the Si_3N_4 by the etching residues is that it varies strongly with the position, making it impossible to characterize the section area of the actuators. A faster etching has been observed in zones only a few microns away from the etched silicon. Under the actuators the etching products are confined, hence an increased etching rate of the silicon nitride is expected. This etching rate can unfortunately not be measured. The only way to estimate it would be with an image of the cross section in TEM but is practically not possible, since it would take an enormous amount of time. Fig. 6.8 shows silicon nitride that has been released by XeF_2 where the etching resulted in thinned edges, to a point where they ended up perforated. This kind of results were observed for the



Figure 6.7: Stress-strain curves obtained for a ZnO sample, with different micro-machine series, on a polyimide sacrificial layer. The bold black line represents a linear elastic behavior with a Young's modulus of 110 GPa obtained from nano-indentation on ZnO thin films.



Figure 6.8: Silicon nitride released with XeF_2 . The Si_3N_4 was etched enough to observe a perforation on its edge.

lab-on-chip fabricated with AZO as a sample layer so it was impossible to obtain a stress-strain curve for this material.

For ZnO it was possible to obtain results for samples deposited with 20%, 27% and 33% oxygen. At higher oxygen concentration the high compressive stress (\sim 1 GPa) created problems due to buckling so no lab-on-chip was obtained. These samples were fabricated with masks, where only the "wide range" series were present. The results are shown in Fig. 6.9. This mask was designed for metals mainly, meaning that it focuses on large deformations. No self-actuated structures are present for the ZnO layer, and no space was designed to allow MOSS measurements. This means that the sample mismatch strain was roughly evaluated by MOSS measurements on similar samples, then adjusted so that the stress-strain curves are aligned with the origin. The mismatch strains were estimated to -0.16, -0.18 and -0.09% (tensile stress) for the samples deposited at 20%, 27% and 33% oxygen respectively.

The stress-strain curves obtained here do not present any surprise since a linear elastic behavior is observed, with a brittle fracture under 1%of strain, and a Young's modulus slightly over 100 GPa in accordance



Figure 6.9: Stress-strain curves obtained with "wide range" structures of lab-on-chip for ZnO deposited at room temperature with 125 mA, 2 mTorr, and 33% (Top), 27% (Middle) and 20% (Bottom) oxygen. Every curve corresponds to a different series.

with nano-indentation and literature. The fracture strain and Young's modulus are not significantly affected by the oxygen concentration since the point defects present in the film are not dominant for the initiation of cracks. For the sample deposited with only 20% oxygen, a slight deviation from a perfect linear elastic behavior is observed. This could be explained by the fact that the ZnO deposited with a low oxygen concentration begins to exhibit metallic behaviors, as it was observed for the electronic and optic properties. TEM observation of such strained samples could demonstrate the presence, or absence of plasticity, in possible Zn clusters. More lab-on-chip could also be produced with the new design to obtain more accurate data and prove, or not, the apparition of plasticity in under-stoichiometric ZnO thin films.

Fig. 6.10 shows how different lab-on-chip series in the new generation of masks give different information with different accuracy. The "wide range" structures have long and large actuators pulling on short and narrow samples, to obtain the whole stress-strain curve, up to the fracture strain (here around 0.6%). At lower deformation (< 0.3%), these structures lead to a large error on the evaluated stress. Structures with larger and longer samples are used to focus on these low deformations with a much better accuracy. The initial strain is evaluated with the self-actuated structures. The unload structures (large sample pulling on a narrow actuator) are used to access the stress-strain curve for strains lower than the mismatch. This sample, was not fabricated with the last set of mask so, even if the different series of mechanical characterization were present, the piezo-resistance could not be measured with the lab-on-chip technique.

Lab-on-chip samples have been produced with the latest design to test the AZO properties. However, as said previously, the silicon nitride used for the actuators was etched during the XeF₂ release. The self actuated structures in AZO have nevertheless been released and the mismatch has been measured for AZO deposited with 13% and 28% oxygen, as deposited and after annealings under Ar for 15 min at 300, 400, 500 and 700°C. The results are shown in Fig. 6.11. The mismatch strain for the non-annealed samples deposited with 13% and 28% oxygen is 0.14% and 0.21% respectively. ZnO has a Poisson ratio of 0.36, and we assume that



Figure 6.10: Stress-strain curve of ZnO deposited with 27% oxygen, obtained with different micro-machines series. Different colors correspond to different micro-machines series. The black and gray solid lines correspond to a linear elastic behavior with a Young's modulus of $105 \pm 5\%$ GPa. The black dot corresponds to the mismatch strain obtained with the self-actuated structures.



Figure 6.11: Mismatch strain evaluated with the self-actuated structures, for AZO samples deposited at room temperature with 13% and 28% oxygen.

AZO has a Young's modulus of 110 GPa, similar to the value obtained for ZnO thin films. During deposition, the MOSS technique measured an average stress of 267 and 432 MPa, leading to an estimated mismatch strain of 0.15% and 0.25%, very close to the value obtained with the self actuated micromachines. This confirms that these two methods allow an accurate evaluation of the internal stress/strain in a thin film. It also confirms that the evaluation of the strain done by X-Rays was here erroneous (see section 5.3.1).

6.6 Conclusions

During this thesis, the lab-on-chip technique has been improved to be suitable for new materials such as ceramics with a low fracture strain. This includes an optimization of the dimensions of the micromachines, but also the inclusion of structures to have a better characterization of the sample material. This optimization of the structures at low deformation is of utmost importance for ceramics, but also for the determination of the Young's modulus of ductile materials.

One major difficulty for ZnO is its amphoteric behavior, meaning that it

is etched in both acidic and basic solutions, strongly limiting the choice of sacrificial layer. A polymer layer had previously been used as sacrificial layer, leading to an infinite selectivity during the release. However, this polymer sacrificial layer has shown that the mechanical anchorage can be poor, leading to incorrect results. The use of XeF_2 and the silicon substrate as sacrificial layer has been proven as a promising way to obtain accurate results for almost all materials, and was successfully applied to obtain the fracture strain and Young's modulus of ZnO thin films deposited with various oxygen concentrations. However, the selectivity between Si and Si_3N_4 is still a major issue and prevented to obtain reliable results for AZO thin films. This problem could probably be solved with the use of silicon oxi-nitride as actuator, combining the tensile stress of silicon nitride and the good selectivity of silicon oxide. When this problem will be solved, the lab-on-chip will allow to easily extract the electro-mechanical properties of almost any free-standing thin film.
Chapter 7

Conclusions and perspectives

This thesis was focused on the study of the deposition by reactive sputtering of ZnO and AZO thin films, and on the improvement of the mechanical testing of thin films, especially for fragile materials.

Aluminum-doped zinc oxide (AZO) is a promising material to replace indium-tin oxide (ITO) as transparent electrodes. Its electrical resistivity is slightly higher than ITO, but it has the advantages of being cheaper and non-toxic, which are very important features for large-scale applications.

Intrinsic ZnO

Chapter 4 described the deposition by reactive sputtering of intrinsic ZnO (iZnO), meaning ZnO without extrinsic dopant. The goal was to study the influence of oxygen concentration during the deposition process on the stoichiometry, the optical, electrical and mechanical properties. This study on intrinsic ZnO allowed a better understanding of the intrinsic defects that are present in ZnO, and growth process that are similar in AZO. The internal stress during growth has been measured with a multi-beam optical stress sensor (MOSS), giving an insight on the possible defects, and growth mechanisms. It was shown that intrinsic defects are not ideal to increase the conductivity of ZnO for several

reasons: they decrease the electronic mobility, increase the optical absorption and are not stables under high temperature, meaning that an annealing, even at only 300°C will make it electrically insulating. Even without annealing, the minimum resistivity was around $4 \times 10^{-2} \Omega.$ cm, more than two orders of magnitude higher than for AZO. Finally, due to the low level of doping, the optical band gap equals the electronic bangap (no Burstein-Moss effect), at only ~ 3.3 eV. iZnO is therefore not suitable for transparent electrodes. In transparent and flexible electronics, it is however important to know the strain present in the devices, meaning that transparent strain gauges are gaining interest. Usual strain gauges are made of metal (gauge factor between 2 and 3) or semi-conductors (between 16 and 45 for polycrystalline silicon). ZnO has here been demonstrated as a potential candidate with a strain gauge comprised between -6 and -8.5, smaller than other usual semi-conductors, but with the advantages of being transparent and deposited at room temperature. The optimal conditions for this application are between the middle and the end of the transition regime ($\sim 33\%$ oxygen), to obtain the largest gauge factor, a high transparency, and a high resistivity but still easily measurable.

Aluminum-doped ZnO

Because iZnO was proven to be inappropriate for transparent electrodes, ZnO with an extrinsic doping was studied in chapter 5. Several doping elements are possible, but aluminum was chosen because it is an abundant element, non toxic, and widely used in doped ZnO. The effect of the aluminum doping on the discharge voltage and the different sputtering regimes (metallic, transition and oxidized) was studied. Thanks to the MOSS and structural characterization (SEM and XRD), growth mechanisms could be studied for different oxygen concentrations and deposition temperatures. It was observed that the middle of the transition regime lead to the best optical and electrical properties. Lower oxygen concentration leads to interstitial zinc that increases the absorption and decreases the electronic mobility. Higher concentrations are not detrimental to the optical properties but highly decrease the electronic density and mobility due to the formation of alumina clusters. An increase of temperature, during or after deposition, enhances the optical and electrical properties due to a decrease of the defects, and an activation of the aluminum dopants. An excessive temperature is however detrimental to the electronic properties due to the formation of alumina clusters. The Young's modulus and hardness was only slightly affected by temperature. However, the hardness decreases when the oxygen concentration increases, possibly due to amorphous, less dense grain boundaries. In summary, the optimal conditions correspond to the middle of the transition regime (20% oxygen here), at a temperature of 180°C, and 2 mTorr to obtain a compact film with a minimum concentration of defects and a maximum of activated dopants, leading to the highest conductivity, transparency and optical bandgap. If the deposition must be done at room temperature an annealing at 300° under argon allows to obtain similar results.

Electro-mechanical lab-on-chip

To test the mechanical properties of the thin films, the lab-on-chip technique has been investigated and optimized for oxide thin films. The challenges were that the observed deformations are small (< 1%), and the study of zinc oxide forbids the use of the hydrofluoric acid usually used during the release with the silicon oxide sacrificial layer. To avoid this problem, a process with a polymer sacrificial layer (polyimide) and an oxygen plasma release was tested. The selectivity with the sample material and actuator was infinite, unfortunately the results were not reproducible and not trustworthy. Using the silicon substrate as sacrificial layer and a release in TMAH was also tested but the selectivity between silicon and zinc oxide was not high enough (<100:1 in optimized conditions). Therefore, a release with XeF_2 and the silicon substrate used as sacrificial layer was investigated. Results could be obtained for ZnO thin films, where a linear elastic and fragile behavior was confirmed (fracture strain of 0.7%), as expected for an oxide. A Young's modulus of 105 GPa was measured, confirming the results given by nano-indentation. For the sample deposited in the metallic regime, the presence of metallic zinc clusters was suspected due to the optical and electrical properties, and could be confirmed by the apparent slight plasticity.

XeF_2 release

Results could unfortunately not be obtained for AZO, mainly due to two problems in the fabrication process. First, despite the release being in a gaseous environment, stiction was observed for the majority of the samples. The origin of this problem is still unknown for the moment. Electrostatic forces can be excluded since stiction was also observed for nickel films short-circuited to the substrate. Thanks to a camera monitoring the release in-situ, it was possible to determine that the stiction occurs during the release, excluding that the stiction comes from the venting of the chamber. Further investigation should be done to understand the origin of this phenomenon and prevent it. The second problem is the selectivity between the silicon substrate and the silicon nitride actuators. Some samples presented an almost infinite selectivity, while others had a selectivity only around 1:100. This selectivity roughly corresponds to a completely etched actuator during the time of the release. Therefore, a selectivity around 1:1000 is the minimum to avoid etching more than 10% of the actuator. There are three possible strategies to enhance the selectivity: optimizing the substrate, optimizing the etching recipe or optimizing the actuator material.

Since the etching of the silicon nitride is not due to XeF_2 but to the silicon etching products, it is important to limit the exposition to these products to increase the selectivity. One possibility is therefore to use SOI substrates to decrease the thickness of the sacrificial layer, and decrease the amount of etched silicon. The use of SOI substrates however favors the stiction due to the thinner sacrificial layer. In the same idea, it could be possible to use nano-porous silicon as a substrate. This could however lead to problems of the mechanical anchorage if the whole substrate is porous. Patterning a localized sacrificial layer of porous silicon before the deposition of the actuator could be problematic since an actuator deposited by CVD would slightly enter the pores. In addition, a process at high temperature on porous silicon tends to oxidize it, which is problematic for XeF_2 releases that are very sensitive to a native oxide. A porosification of silicon after the deposition and patterning of the actuators would only slightly decrease the amount of etched silicon and the release time, since the parts to under-etch would still mainly be composed of bulk silicon. In addition, the porosification process would expose the actuators to concentrated HF, hence etch them significantly. A final possibility would be to increase the etching rate of silicon to decrease the time needed to etch the same amount of silicon, hence decrease the exposition to the etching products. P-type silicon substrates have been tested and a highly decreased etching rate has been observed. Lab-on-chip on highly n-doped silicon must still be tested, but should allow to decrease the release time of a factor 2, as reported in the literature. [162]

As discussed in section 3.7 with more details, some other gas can be added during the release to increase the selectivity. The mechanisms are not clear yet, but a higher thermal conductivity seems to cool down the sample that heats due to the exothermic etching, and a lower temperature would increase the selectivity. Attention must be paid to the added gas since is can react with the fluorine and deposit some fluorinated polymer on the surface of the sample. This was particularly observed with water. In this work, we observed that an easy and efficient way of increasing the selectivity is to make the etching with pulses of a shorter duration, so that the etching products are pumped away faster. To increase even more the selectivity, it is possible to do a purge at the end of each pulse with another gas such as nitrogen, to evacuate more efficiently the etching products.

The third and final strategy to increase the selectivity is to optimize the actuator. As explained in chapter 6, Si_3N_4 has been chosen as actuator because of its optimal mechanical behavior, thermal and chemical stability, and high tensile stress after deposition. However, with the XeF_2 release the chemical stability is not sufficient. We observed that a passivation layer can be created at the surface of the silicon nitride, by an annealing in oxygen, or by exposition to an oxygen plasma. This passivation layer is very slowly etched, but extremely thin and is eventually etched, exposing the silicon nitride that is etched must faster. An

additional problem is that this layer can not be created at the end of the process because it would also oxidize the silicon surface, making the release impossible due to the sensitivity of XeF₂ to native oxide. To obtain an homogeneous release, it is actually better to remove the native oxide with an argon plasma but this plasma also damages the passivation layer of the actuators, decreasing the selectivity. Therefore, a future perspective is to investigate the use of silicon oxynitride (Si₃O_{ε}N_{4- ε} with a small ε). The incorporation of oxygen seems to extremely improve the selectivity, as it was was suggested by one sample that might have been exposed to a water leak during the CVD process, and exhibited an almost infinite selectivity. The amount of oxygen must however be small because silicon oxide exhibits compressive stress, which is not usable for actuators. Finally, another possibility is to use an other material for the actuators than silicon nitride.

Alternative actuators

LPCVD silicon nitride is an ideal actuator if we consider its mechanical properties. However, its high temperature deposition imposes several restrictions that can be problematic for the testing of several materials.

This could be avoided with the use of metallic actuators deposited at room temperature. Several tests have been carried out during this thesis, with platinum, palladium and nickel as actuators. The advantage of these actuators is that they can be deposited at room temperature, after the deposition of the sample. If the sample must be annealed to obtain certain properties, it can be done without impacting the actuator since it can be deposited at the end of the fabrication process. Another advantage of platinum and palladium as actuators is their high chemical stability, meaning that they can be used in the four different available processes (release with HF, oxygen plasma, TMAH, or XeF₂).

Depending on the tested material, the adhesion between the sample and the actuator can also be improved with a metallic actuator instead of silicon nitride. This was for example observed for graphene where nickel actuators seem to have a higher adherence than silicon nitride. The major drawback of metallic actuators is their mechanical properties. Self-actuated lab-on-chip have been successfully produced for platinum and palladium with the XeF₂ process and the results for Pt are presented in Fig. 7.1. The results for palladium are not presented since this material has already been extensively studied in a previous thesis [163] and only the compatibility with the XeF₂ process has been tested in this thesis. It can be seen for platinum that plasticity is present, and there is stress relaxation occurring after only a few days, as it was observed for palladium thin films. However, if platinum or palladium were used as actuators, the applied strain would be small (<0.3%), where plasticity and stress relaxation should be small too. To analyze more accurately the mechanical properties of Pt thin films, lab-on-chip should be produced with Si₃N₄ actuators to test it, especially at low deformation levels.

If the mechanical properties of the actuators are not well known, the problem is that it is not possible to evaluate the stress in the sample. However, even if it is not possible to obtain the stress-strain curve, it is still possible to apply a strain and characterize the strained sample with other techniques such as TEM, Raman, or cathodoluminescence for example.

The platinum layer in this test was deposited by e-beam evaporation and exhibited high tensile stress (between 1.2 and 1.5 GPa), that often caused delamination or cracking during the release. To avoid this, an annealing can be done at 200°C for 24 hours (a higher temperature would create platinum silicide due to a reaction with the substrate) to decrease the internal stress to about 1 GPa. Palladium exhibits lower internal stress, between 150 and 850 MPa depending on the deposition rate and therefore does not present cracking during the release. A method to have a better control on the internal stress would be a deposition by sputtering, where the stress can be controlled with the pressure, and monitored with the MOSS technique.

Lab-on-chip were also produced with silicon nitride actuators and nickel samples. Unfortunately, the actuators were heavily etched during the release, meaning that the stress could not be calculated. The only conclusions that could be drawn are that nickel thin films are compatible with the XeF₂ process and that the measured sample had an almost lin-



Figure 7.1: Stress-strain curve obtained with self-actuated lab-onchip, for a 50 nm-thick platinum film, as deposited and after 6, 19 and 33 days.

ear elastic behavior up to about 0.5%, then a plastic behavior with deformations up to 4.7%. Note that this sample had relatively low internal stress ($\simeq 450$ MPa) that could be obtained thanks to a tuning of the pressure during deposition by sputtering. In an other thesis presented in 2018 [164], attempts to produce lab-on-chip with nickel samples were unsuccessful, partly because the internal stress was too high, leading to a premature fracture of the samples. Even though the stress-strain curve could not be obtained, it was obvious that the fracture strain was far bellow 5%, meaning that very low plasticity was present. This could be explained because films with higher stress levels generally contain more defects, hence have a more fragile behavior. Nickel thin films deposited by sputtering could therefore be used as actuators, after an optimization of the deposition conditions (mainly power and pressure) to obtain high internal stress (not too high to avoid delamination and cracking) and a high elastic limit. Note that a stress gradient is often observed, with a nucleation layer in compression. This nucleation layer (thickness on the order of 5 nm) with compressive stress could be a problem for very thin actuators, where the stress gradient would generate a large out-of-plane displacement.

Lab-on-chip with graphene specimen

As said in the introduction, transparent conductive oxides (TCOs) are now the dominant class of materials for transparent electrodes. Graphene could become interesting for this application due to its high transparency, potentially low resistivity if doped, and theoretically high elastic limit. However, the production and transfer of large areas of high-quality graphene, is still problematic. In addition, its exceptional mechanical behavior has been predicted theoretically but its experimental mechanical testing still remains a major challenge. [165] Recently, two PhD theses were presented at UCL about graphene, one focusing on the mechanical testing [166] and one focusing on the synthesis by CVD [167]. Since graphene could be of major interest for future transparent electrodes, some tests were performed to apply the lab-on-chip technique to graphene, based on the previous experience. The process defined by Hammad was as follows (for details, see Ref. [166]):

- Deposition of copper sacrificial layer
- Transfer of graphene on the sacrificial layer
- Pattering of the graphene by O₂ plasma etching
- Possible oxidation of the graphene to improve adherence with the actuators
- Deposition of the PECVD silicon nitride actuators
- Patterning of the actuators by wet etching
- Spin-coating and patterning of photoresist on top of the graphene beams to protect them during the release
- Release by wet etching of the copper in APS, rinsing, and removal of the photoresist with acetone or PG remover

• Critical point dryer

This process was adapted from the original process to overcome several difficulties due to the graphene, but still had several problems that made unsuccessful the attempts to produce lab-on-chip.

First, transferring graphene from the original substrate to a substrate with a sacrificial layer is challenging because large areas need to be transferred, and micro-cracks occur during the transfer. In addition, transferred graphene usually exhibits a poor adhesion after transfer. Therefore, it is impossible to test the mechanical properties since almost all the specimens are already broken before the release. Therefore, in this thesis, we used the copper thin film used as catalyst, as a sacrificial layer too. However, this solution was problematic too because the copper used as catalyst is heated near its fusion point, hence exhibits high roughness, especially at the grain boundaries that form deep rifts. These rifts are then imprinted in the actuators and the graphene deposited on top, highly favoring the apparition of cracks. After the tests were performed some improvements were done in the synthesis of graphene, leading to almost single crystal copper sacrificial layer when sapphire is used as substrate, which should fix that problem.

A second major problem is the poor adhesion between graphene and the silicon nitride actuators. Slightly oxidizing the graphene with a plasma seems to improve the adhesion, but gives poorer properties since the graphene is oxidized. In the previous thesis [166], the graphene was slightly oxidized on its whole surface, then the silicon nitride was deposited on top and patterned by wet etching. Here we propose the use of nickel actuators because of the better adhesion on graphene. In addition, to increase the contact surface hence the adhesion, we propose to keep graphene under the whole actuator. In our sputtering equipment it is also possible to apply an oxygen plasma on the sample just before the deposition of the actuator. This means that the actuator is deposited on a perfectly clean and slightly oxidized surface, improving further more the adhesion. If the actuator is patterned by lift-off and the slight oxidation is done just before the actuator deposition, is also means that only the part under the actuator is oxidized, leaving pristine graphene in the specimen part of the micro-machine.

A third difficulty is that graphene is easily damaged during the release, therefore it was proposed to deposit and pattern photoresist on top of the graphene beams to ensure a mechanical reinforcement. It was previously done with a third lithography, after the patterning of the graphene, and of the actuators. An additional difficulty was the alignment of this protective layer with the specimens. If the actuators are deposited on the unpatterned graphene and only then the graphene is patterned by plasma, the photoresist can be used both as the mask and the mechanical support that is perfectly aligned with the specimen. Note that the photoresist is slightly cross-linked at its surface due to the plasma used to pattern the graphene, and this cross-linked layer is difficult to remove during the release. Indeed, the best way to remove this layer is with agitation of the solution, but it can not be done on released graphene without damaging it. Therefore, it is possible to spin-coat a layer of PMMA between the photoresist and the graphene, to help removing the residues in acetone as shown in the previous thesis. An other possibility to remove these residues would be to spin-coat PMMA, then photoresist, make the lithography, pattern the PMMA and graphene in an oxygen plasma, expose the whole wafer to UV, and remove the remaining photoresist in the developer (diluted TMAH). That way, the photoresist could be rinsed away with agitation since the structures are not released yet, and it would leave the PMMA intact that can be used as mechanical reinforcement. This was however not tested, so the sample that we realized presented the residues on most parts of the lab-on-chip, as it can be seen in Fig. 7.2. If no agitation is possible, making the release with the sample tilted at 90° improves the results since, simply by gravity, the residues tend to fall off the substrate instead of re-deposit on the sample.

What was observed in this thesis and in the previous thesis on mechanical testing of graphene [166] is that a high amount of graphene beams are broken, even at low deformation, even if great care is taken during the release to minimize the turbulence in the solution. An origin of this phenomenon could be explained with the photoresist used as mechanical support. Indeed, we released some micro-machines with photoresist on



Figure 7.2: Preliminary tests of a new process for graphene labon-chip. (Top) A film of hardened photoresist redeposited on the sample, but is partially removed and allows to see the graphene specimen between two nickel actuators. (Bottom) The residue did not redeposit because the sample was tilted during the release. The lighter lines correspond to grain boundaries in the copper sacrificial layer. No CPD was done on these samples.

top of the graphene, and did not remove the photoresist after the release. What we observed is that in most cases when an actuator pulls on the photoresist, it breaks, and breaks the graphene under it. To avoid this, we recommend to do the release at higher temperature (around 80°C) to allow a stress relaxation in the photoresist during the release. Using PMMA only as mechanical reinforcement should also help with this problem due to its higher fracture strain.

Finally, with all these observations we propose an improved process to produce lab-on-chip with 2D materials such as graphene, that could be a promising material for future transparent electrodes.

- CVD deposition of graphene on copper thin film on a sapphire substrate.
- Lift-off lithography to pattern the actuators.
- Light oxygen plasma (improved adhesion) and deposition of nickel actuators by sputtering (control of the internal stress). Lift-off in acetone.
- Spin-coating of PMMA (mechanical support for the release) and positive lithography to pattern the graphene specimens.
- Oxygen plasma to pattern the PMMA and graphene.
- Removal of the photoresist with full UV exposure and dissolution in developer (diluted TMAH).
- Release in APS heated at 80°C (softening of the PMMA), rinsing in water, IPA, and acetone.
- Critical point dryer.

 ${}_{\text{Appendix}} \, {\bm A}$

Complementary figures



Figure A.1: Evolution of the product Stress× Thickness as a function of the deposited thickness, for different oxygen concentrations (Top), and different deposition temperatures (Bottom). For the samples heated during deposition, the cooling down has been recorded to have the average stress at room-temperature.



Figure A.2: Charge carrier mobility (Top) and density (Middle), and resistivity (Bottom) of AZO samples deposited at various oxygen concentrations and annealed at various temperatures under argon atmosphere, for 15 min.

Appendix **B**

List of publications

Journal Publications

- R. Tuyaerts, O. Poncelet, J-P. Raskin and J. Proost. Internal stress and opto-electronic properties of ZnO thin films deposited by reactive sputtering in various oxygen partial pressures. *Journal* of Applied Physics - Vol. 122, p. 155306 (2017)
- J. Proost, F. Henry, R. Tuyaerts and S. Michotte. Effect of internal stress on the electro-optical behaviour of Al-doped ZnO transparent conductive thin films. *Journal of Applied Physics - Vol. 120*, p. 075308 (2016)
- O. Poncelet, J. Rasson, R. Tuyaerts, M. Coulombier, K. Ratan Raja Venkata, J-P. Raskin and L. Francis. Hemispherical cavities on silicon substrates: an overview of micro fabrication techniques. *Journal of Applied Physics - Vol. 120, p. 075308 (2016)*
- 4. R. Tuyaerts, J-P. Raskin and J. Proost. Effect of oxygen concentration, deposition temperature and annealing, on the optoelectrical properties and internal stress in AZO thin films deposited by DC reactive sputtering. *Journal of Applied Physics - Submitted*

Conference Publications

- R. Tuyaerts, F. Henry, J-P. Raskin and J. Proost. Strain-engineered piezoelectric ZnO thin films. 8th International Workshop on Zinc Oxide and Related Materials, Symposium on Piezoelectric, Acousto-Optic, Gas, Chemical and Biosensor Device Applications - Ontario, Canada (2014)
- J. Proost, F. Henry, F. Van Wonterghem, R. Tuyaerts, S. Michotte. What strain can (or cannot) do to your TCO. 2015 Fall Meeting of the European Materials Research Society (E-MRS), Symposium on Transparent Conductive Materials : from Fundamental Understanding to Applications - Warsaw (2015)
- R. Tuyaerts, J-P. Raskin and J. Proost. Electromechanical testing of ZnO thin films under high uniaxial strain. The 30th International Conference on Microelectronic Test Structures - ICMTS 2017 - Grenoble, France (2017)

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